

# Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests

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*Critical loads for N deposition effects on lichens, trees and nitrate leaching provide benchmarks for protecting California forests.*

## Abstract

Empirical critical loads (CL) for N deposition were determined from changes in epiphytic lichen communities, elevated  $\text{NO}_3^-$  leaching in streamwater, and reduced fine root biomass in ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.) at sites with varying N deposition. The CL for lichen community impacts of  $3.1 \text{ kg ha}^{-1} \text{ year}^{-1}$  is expected to protect all components of the forest ecosystem from the adverse effects of N deposition. Much of the western Sierra Nevada is above the lichen-based CL, showing significant changes in lichen indicator groups. The empirical N deposition threshold and that simulated by the DayCent model for enhanced  $\text{NO}_3^-$  leaching were  $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . DayCent estimated that elevated  $\text{NO}_3^-$  leaching in the San Bernardino Mountains began in the late 1950s. Critical values for litter C:N (34.1), ponderosa pine foliar N (1.1%), and N concentrations (1.0%) in the lichen *Letharia vulpina* (L.) Hue are indicative of CL exceedance. Published by Elsevier Ltd.

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## 1. Introduction

Globally humans have altered the nitrogen (N) cycle to a greater degree than the much more publicized carbon cycle. As nitrogen (N) compounds cascade through the environment, there are many effects on the environment and aquatic and terrestrial ecosystems (Galloway et al., 2003). A major objective of research efforts on the impacts of N deposition is to quantify the N deposition inputs at which unacceptable impacts occur to sensitive ecosystem components. The critical loads (CL) approach has been widely used to determine the threshold deposition inputs above which unacceptable impacts begin to occur. The use of CL promises to be instrumental as

we progress towards air quality management and regulation more firmly rooted in ecosystem protection. Critical loads can be determined for acidification or eutrophication effects in both aquatic and terrestrial ecosystems. Nitrogen and sulfur deposition both contribute to soil acidification effects, while eutrophication or N enrichment effects in terrestrial ecosystems are caused by N deposition. In this study we focus on eutrophication responses although considerable soil acidification has also occurred in high deposition areas in the San Bernardino Mountains (Breiner et al., 2007; Wood et al., 2007).

The largest coordinated effort in developing and implementing CL has been the efforts of the United Nations – Economic Commission for Europe, International Cooperative Programme (UNECE ICP, 2004). These methods have been adopted by researchers in other countries as well. In the United States there are no large coordinated programs to establish

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suitable CL and no regular extensive and intensive monitoring efforts designed to evaluate CL methodologies. However, projects for developing CL are increasing in North America and a wide variety of approaches have been used in both Canada and the US (Baron, 2006; Ouimet et al., 2006; McNulty et al., 2007; Porter and Johnson, 2007; Williams and Tonnessen, 2000).

The principal methods for CL determination include steady state simple mass balance models (SMB), dynamic models, and empirical observations. Empirical methods are based on site specific data showing deposition levels at which “harmful” biological effects are observed (Bobbink et al., 2003). A major limitation of the empirical approach is that results may only be applied with confidence to sites with highly similar biotic and environmental conditions. Empirical CL are important, however, for validating CL values determined indirectly with SMB and dynamic simulation models. Empirical CL are based on realistic conditions under which adverse biological impacts occur. Simulation modeling methods are particularly useful for evaluating the effects of different combinations of deposition levels, temporal dynamics, disturbance regimes, stand characteristics, and other variables on CL.

The SMB model is the most widely applied CL method in the ICP European network (UNECE ICP, 2004). Models such as the SMB are used to map CL at large scales, but must make many assumptions regarding nutrient cycling and soil chemical processes and lack the resolution to provide accurate site-specific CL. The approach is thus best applied over broad regions. Even when the SMB model is parameterized with site specific data, the capacity of the SMB models to provide reliable estimates of the CL for soil acidification or eutrophication has been questioned (Cresser, 2000; Rodriguez-Lado et al., 2007; Skeffington, 1999), and the biological linkages for the calculated CL are even more uncertain in many cases unless verified by empirical or mechanistic data (De Vries et al., 2007; UNECE ICP, 2004). Notwithstanding the widespread use of relatively standardized CL methodologies in Europe and elsewhere, questions still remain regarding the best approach for determining CL that reflect ecologically relevant thresholds of N deposition.

The major objectives of this study are to determine the ‘N as a nutrient’ CL for key endpoints in mixed conifer forests in California and to compare different empirical and modeling approaches for determining the N as a nutrient CL. Empirical CL were determined for effects on lichen communities and for  $\text{NO}_3^-$  leaching in association with previously published results on reduced fine root biomass (Grulke et al., 1998) from sites spanning N deposition gradients. Epiphytic lichens are among the most sensitive bioindicators of N in forested ecosystems (Blett et al., 2003; Bobbink et al., 2003; Fenn et al., 2003b; Glavich and Geiser, in press). Consequently, the implementation of lichen-derived CL is likely to prevent undesired impacts to the broader forest ecosystem. Protecting the integrity of lichen communities, moreover, ensures preservation of their complex ecological roles in the nutrient cycling, hydrological flux and supply of wildlife forage and nesting

materials to the forest (McCune et al., 2007). Finally, information on CL will be discussed in regard to their implications for resource protection and land management.

## 2. Materials and methods

### 2.1. Site locations

Twenty-four mixed conifer forest sites in California exposed to a wide range of N deposition inputs (Fig. 1; Table 1) were included in this study. Dominant overstory species were ponderosa pine (*Pinus ponderosa* Laws) or Jeffrey pine (*P. jeffreyi* Grev. and Balf.) and commonly associated species included California black oak (*Quercus kelloggii* Newb.), white fir (*Abies concolor* Gord. & Glend.), and incense cedar (*Calocedrus decurrens* (Torr.) Florin). Fifteen sites were located in the Sierra Nevada Mountains and nine in the San Bernardino Mountains. The primary use of these forests is recreational and protection of habitat and water sources. Little known logging has occurred in the study sites since the early 20th century, and except for fires that occurred in the vicinity of some of the San Bernardino Mountain sampling sites in the fall of 2003, the sites have not been affected by fire in the last 70 years. In all instances, we did not collect samples close to burned areas. Soil parent material is weathered or decomposed granitic rock, except at Lassen where the soil is of volcanic origin. The soils are generally sandy loam in texture and percent base saturation ranges from 70 to 100% (Fenn et al., 1996) except in the most polluted western San Bernardino Mountain sites where base saturation has decreased in recent years. Nitrogen deposition in canopy throughfall was measured year-round at the Sierra Nevada sites for one or two years from 2000 to 2003 (Fenn et al., 2003a,c; and M.E. Fenn, unpublished data) and in the San Bernardino Mountains sites for 2–5 years from 2000 to 2005 (Fenn and Poth, 2004; Fenn et al., 2003a; and M.E. Fenn, unpublished data). Throughfall fluxes were measured using ion exchange resin throughfall collectors (Fenn and Poth, 2004). The deposition data do not include deposition fluxes during fire episodes.

### 2.2. Empirical critical load for nitrate leaching and fine root biomass impacts

The empirical threshold for  $\text{NO}_3^-$  leaching is based on the relationship between throughfall N deposition and an empirically-derived clean-site threshold value for streamwater  $\text{NO}_3^-$ . The threshold was derived by comparing temporal profiles of streamwater  $\text{NO}_3^-$  concentrations in relatively pristine low N deposition catchments against profiles of catchments receiving varying levels of chronic N deposition inputs. Based on 28 streams from relatively low pollution catchments in southern California (Fenn and Poth, 1999; Riggan et al., 1985) we determined that peak  $\text{NO}_3^-$  concentrations in runoff rarely exceed  $0.2 \text{ mg NO}_3\text{-N L}^{-1}$  ( $14.3 \mu\text{M}$ ). This concentration corresponds with those reported for relatively unpolluted streams in Sweden (De Vries et al., 2007). Thus, we selected  $14.3 \mu\text{M}$  as the critical threshold value for identifying catchments that are beginning to exhibit symptoms of N excess or N saturation. The empirical N threshold for  $\text{NO}_3^-$  leaching is thus the N deposition input at which this threshold peak  $\text{NO}_3^-$  concentration is exceeded.

The N deposition input leading to  $\text{NO}_3^-$  leaching was determined by a linear regression equation between throughfall N deposition and streamwater  $\text{NO}_3^-$  data collected from 11 sites in the San Bernardino and southern Sierra Nevada Mountains encompassing a range of annual N deposition inputs ( $5.7\text{--}71.1 \text{ kg ha}^{-1} \text{ year}^{-1}$ ). Streamwater samples were collected as grab samples ( $n = 3$  per sampling date) during two surveys done in February and March 2007, when runoff rates were highest. The throughfall sampling site within each of the 11 catchments was located in the mixed conifer zone. Accessible stream sampling sites were in the mixed conifer zone at 7 of the sites (SL, GF, CA, BF, GV, HP, GH; Table 1) or at lower elevation scrub oak or chaparral sites in 4 of the catchments (MH, PI, BR, CP; Table 1). An implied assumption in developing an empirical CL associated with  $\text{NO}_3^-$  leaching is that atmospheric deposition is the sole source of elevated runoff  $\text{NO}_3^-$ . In selecting streamwater sampling sites for CL determinations, catchments disturbed by

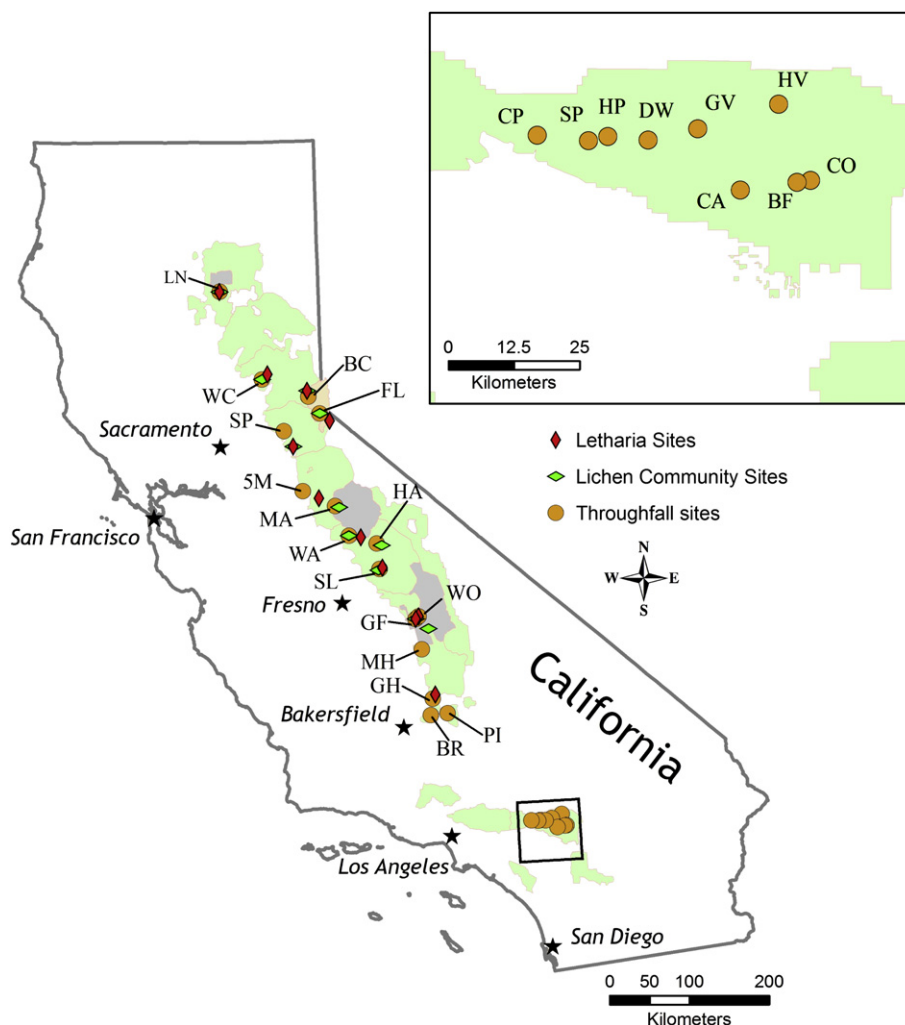


Fig. 1. Map of sampling sites in the Sierra Nevada and San Bernardino Mountains in California. The green shaded areas represent national forests and the grey shaded areas represent national parks. For a list of site names see Table 1.

forest fires, stand thinning, or other anthropogenic activities that stimulate net nitrification or otherwise release  $\text{NO}_3^-$  to the system were excluded.

Because a CL by definition refers to atmospheric inputs causing a harmful biological effect, we tested the relationship between reduced fine root biomass in ponderosa pine (see Grulke et al., 1998) and streamwater  $\text{NO}_3^-$  concentrations or N deposition at sites across the N deposition gradient in the San Bernardino Mountains. This linkage must be considered preliminary because the fine root data are only available from three sites (Grulke et al., 1998), although the sites span a N deposition range of 7.5, 39.3, and  $71.1 \text{ kg ha}^{-1} \text{ year}^{-1}$ . The reduction in fine root biomass is dramatic with increasing air pollution exposure and is strongly correlated with streamwater  $\text{NO}_3^-$  ( $r^2 = 0.75$ ) and N deposition ( $r^2 = 0.82$ ; Table 2). Further work at a greater number of sites will be needed to verify the quantitative nature of the response of fine roots to N enrichment. Ozone is also believed to contribute to the decreased C allocation to fine roots (Grulke et al., 1998) and could be considered as a confounding factor. However, inasmuch as the intent of the empirical CL is to estimate the N deposition level at which harmful effects occur to the ecosystem under realistic field conditions, ozone exposure effects should be included because in California forests ozone and N are co-occurring pollutants.

### 2.3. Litter C:N as a predictor of the N deposition CL

Litter was sampled under five ponderosa or Jeffrey pine trees at a subset of the study sites (LN, SL, GF, MH, CP, SP, DW, CO). Litter was collected at two

diametrically opposed points located at approximately the midpoint of the radius from the stem of a mature tree to the canopy drip line. The entire depth of the forest floor or organic horizon was sampled except for the undecomposed superficial L-layer litter. Litter from the two sampling points per tree was combined into one replicate sample. The samples were analyzed for total C and N by standard combustion methods with a Carbo Erla analyzer (Fenn et al., 1996).

### 2.4. Empirical critical loads for lichen responses

A preliminary CL for lichens of mixed conifer forests in the Sierra Nevada was developed by cross-walking throughfall N measurements with N concentration in *Letharia vulpina* (Fig. 2) and indices describing lichen community composition ( $n = 11$ ). Nitrogen concentration in *L. vulpina* represents an easily measured biological response to N that correlates closely with local deposition. An abundance of *L. vulpina* data from forests in the Pacific Northwest allowed us to compare collections spanning from polluted to remote sites and determine natural ranges for lichen N concentrations. With this information we defined a “clean site” threshold for N enhancement (analogous in concept to the threshold value used for streamwater  $\text{NO}_3^-$ ; see Section 2.2), which we used to anchor the lichen CL. Lichen samples were collected between 1994 and 2004 primarily from forests on the east side of the Cascade Crest. Sampling and laboratory protocols followed Geiser (2004). Raw data are available on-line at <http://gis.nacse.org/lichenair>. Laboratory and field replicates were averaged for each site visit, yielding a final sample size of



Table 1  
Throughfall N deposition ( $\text{kg ha}^{-1} \text{ year}^{-1}$ ) at 24 sites from the Sierra Nevada and San Bernardino Mountains

Site	Coordinates		N deposition
Sierra Nevada Mountain sites			
(LN) Lassen	40° 19' 1.20"	121° 26' 27.60"	1.4
(WC) White Cloud	39° 18' 59.01"	120° 50' 55.80"	7.2
(BC) Blackwood Canyon	39° 06' 45.00"	120° 10' 60.00"	1.2
(FL) Fallen Leaf	38° 55' 4.00"	120° 01' 40.00"	1.6
(SP) Sly Park	38° 43' 48.00"	120° 32' 60.00"	3.1
(5M) Five Mile	38° 02' 60.00"	120° 17' 60.00"	4.2
(WA) Wawona	37° 31' 48.00"	119° 40' 12.00"	3.3
(SL) Shaver Lake	37° 08' 33.95"	119° 15' 09.10"	5.7
(WO) Wolverton	36° 35' 38.40"	118° 44' 13.20"	5.0
(GF) Giant Forest	36° 34' 00.84"	118° 46' 37.92"	10.1
(HHA) Hell's Half Acre	37° 25' 58.37"	119° 16' 45.07"	7.2
(MH) Mountain Home	36° 13' 23.28"	118° 42' 46.84"	13.5
(BR) Breckenridge	35° 28' 33.15"	118° 37' 34.71"	15.0
(PI) Piutes	35° 29' 31.65"	118° 23' 44.95"	9.5
(GR) Greenhorne	35° 39' 42.42"	118° 35' 24.40"	18.3
San Bernardino Mountain sites			
(HV) Holcomb Valley	34° 17' 35.27"	116° 54' 43.15"	6.1
(CO) Camp Osceola	34° 09' 43.54"	116° 51' 26.77"	7.5
(GV) Green Valley	34° 15' 04.11"	117° 03' 02.36"	8.7
(BF) Barton Flats	34° 09' 33.48"	116° 52' 49.15"	8.8
(CA) Camp Angelus	34° 08' 43.87"	116° 58' 40.75"	12.8
(DW) Dogwood	34° 14' 14.62"	117° 12' 18.40"	33.4
(HP) Heaps Peak	34° 13' 53.74"	117° 08' 09.19"	36.4
(SP) Strawberry Peak	34° 13' 49.63"	117° 14' 18.31"	39.3
(CP) Camp Paivika	34° 14' 23.95"	117° 19' 34.22"	71.1

535. A small number of sites were sampled in both 1994 and 2004; these were treated as independent measurements.

A smooth curve was fitted (kernel standard of 0.0883) to a histogram of the distribution of N concentrations in all 535 samples. The fitted distribution showed a major peak (Fig. 3) representing the clean sites, which made up the bulk of samples. Values in the skewed upper portion of the distribution represent the enhanced-N population (i.e., sites affected by local agricultural or urban—industrial emissions). Confirmation that “clean sites” were exposed to relatively low N levels was evident in composition of the epiphytic lichen communities, namely, in the absence of nitrophytic lichens and the presence of

Table 2

Linear regression equations used to derive the empirical threshold for streamwater  $\text{NO}_3^-$  loss and equations for key ecosystem N status indicators related to  $\text{NO}_3^-$  leaching and the empirical CL for fine root biomass reduction

Parameters <sup>a</sup>	Regression equation	$r^2$	Number of sites sampled
Throughfall N deposition (y) vs. streamwater $\text{NO}_3^-$ (x)	$y = 8.69 + 0.58x$	0.98	11
Bulk N deposition (y) vs. streamwater $\text{NO}_3^-$ (x)	$y = 4.07 + 0.05x$	0.72	8
Throughfall N deposition (y) vs. litter C:N (x)	$y = 148.08 - 3.81x$	0.79	8
Litter C:N (y) vs. streamwater $\text{NO}_3^-$ (x)	$y = 35.65 - 0.11x$	0.74	6
Fine root biomass (y) vs. throughfall N deposition (x)	$y = 0.81 - 0.012x$	0.82	3
Fine root biomass (y) vs. streamwater $\text{NO}_3^-$ (x)	$Y = 0.68 - 0.0068x$	0.75	3

<sup>a</sup> Units for throughfall and bulk N deposition are  $\text{kg ha}^{-1} \text{ year}^{-1}$ . Streamwater  $\text{NO}_3^-$  concentrations are as  $\mu\text{eq L}^{-1}$ , and fine root biomass are g per soil pit ( $20 \times 20 \text{ cm}$ ; only data from the top 20 cm are included here) (Grulke et al., 1998).



Fig. 2. *Letharia vulpina*, or wolf lichen, is a broadly distributed epiphyte in western montane forests. Nitrogen (N) concentrations in this lichen are correlated with both N deposition and adverse changes in lichen community composition, making it a simple and useful tool in critical loads development and indication of critical load exceedances. Top: Habitat on trunks of white fir (*Abies concolor*) in Sequoia National Park, elev. 2100 m. Bottom: Close-up; numerous fine branches of *L. vulpina* create an extensive surface area, facilitating accumulation of wet and dry N deposition.

air pollution sensitive species (see also distribution maps of sensitive and N indicator lichens in Oregon and Washington presented in Fenn et al., 2003b, 2007).

We calculated a clean site threshold value of 1.0% N (Fig. 3). This threshold represents the uppermost limit, or 100% quantile, of the expected range of values for % N in *L. vulpina* collected from clean sites. Assuming that concentrations of N in lichens from clean sites follow a normal distribution and that most sites were clean, the peak density of the fitted curve, 0.60% N was used to represent the 50% quantile for the clean sites. The skewed upper part of the distribution represents samples from N enhanced sites. The 100% quantile for % N in the clean population was then calculated by doubling the distance between the 0% quantile (0.20% N) and the 50% quantile, i.e.  $2 \times (0.60\% \text{ N} - 0.20\% \text{ N}) = 1.0\% \text{ N}$ . Nitrogen concentrations above this threshold are considered enhanced.

#### 2.4.1. Ecological effects on lichens

The clean-site threshold is a pragmatic anchor for the lichen CL because it serves to capture the lower bound in a series of ecologically-based CL that correspond with major shifts in Sierra Nevada lichen communities. These shifts are described using Forest Inventory and Analysis (FIA) data that are

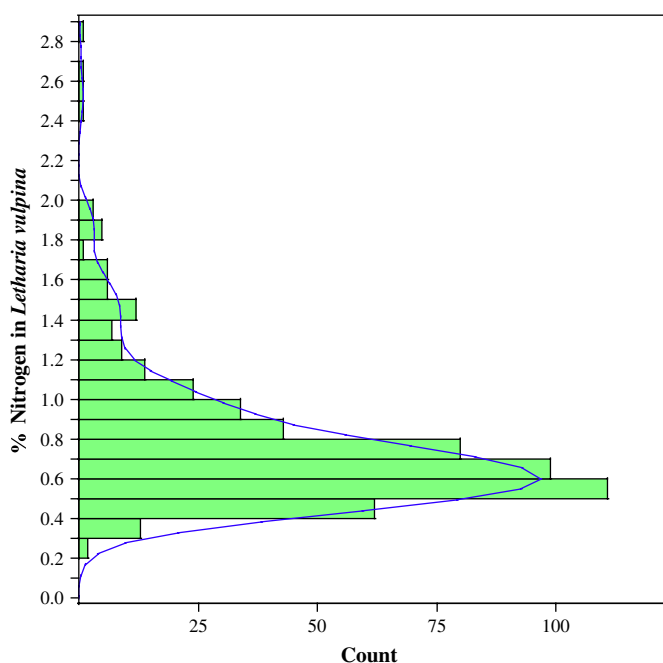


Fig. 3. Histogram of % N in *Letharia vulpina*, dry weight, sampled from urban, rural, and remote Oregon and Washington forests east of the Cascade Crest between 1994 and 2004 ( $N = 535$ ). Two populations, clean and N-enhanced, were apparent when we fit a smoothed distribution (blue line) to the histogram. Assuming that concentrations of N in lichens from clean sites follow a normal distribution and that most sites were clean, the peak density of the fitted curve, 0.60% N was used to represent the 50% quantile for the clean sites. The skewed upper part of the distribution represents samples from N enhanced sites. The 100% quantile for % N in the clean population was then calculated by doubling the distance between the 0% quantile (0.20% N) and the 50% quantile, i.e.  $2 \times (0.60\% \text{ N} - 0.20\% \text{ N}) = 1.0\% \text{ N}$ . The 100% quantile, 1.0% N, was selected as the upper limit for the expected background range, or 'clean site threshold.' Nitrogen concentrations above this threshold are considered enhanced.

collected on a systematic grid of permanent plots. The FIA data consist of 2 h ocular surveys during which a trained observer collects specimens of each epiphytic macrolichen found within a 0.38 ha plot (USDA FS, 2005). Each species is assigned a broad abundance code: 1, rare (<3 thalli); 2, uncommon (4–10 thalli); 3, common (>10 thalli but covering <50% of all boles and branches); 4, abundant (>10 thalli and covering >50% of all boles and branches). Protocol and repeatability are discussed in McCune et al. (1997).

Lichen species respond differentially to N, which allows species to be categorized into three N indicator groups based on their N sensitivity (Geiser and Neitlich, 2007; Jovan, 2008; Jovan and McCune, 2006) and Western Europe (Lambley and Wolseley, 2004; Sparrius, 2007; van Herk, 2001): acidophytes, neutrophytes, and nitrophytes (Table 3). Acidophytes are sensitive to even small enhancements in N deposition (van Herk et al., 2003) and will eventually disappear from the lichen community under continued N loading. This ecologically significant group includes the 'beard lichens' and other species utilized by wildlife for forage and nesting material in the Sierra Nevada (McCune et al., 2007). By contrast, neutrophytes are either tolerant or, in some cases, enhanced by N deposition although never becoming "weedy" like nitrophytes. Nitrophytes are fast-growing species associated with ammonia ( $\text{NH}_3$ ) deposition as well as substrates with relatively high pH, such as many hardwoods.

Four plot-level indices were calculated using the lichen community data based on the proportion of lichen abundance in a particular N indicator group: (1) the proportion of total lichen abundance in acidophytes (PAA in Eq. (1)); (2) the proportion of total lichen abundance in neutrophytes; (3) the proportion of total lichen abundance in nitrophytes; and (4) acidophyte dominance (acidophyte index minus neutrophyte index).

$$\text{PAA}_i = \frac{\sum_{j=1}^s a_{ij} I_j}{\sum_{j=1}^s a_{ij}} \quad (1)$$

where  $s$  is the number of species in plot  $i$ ,  $a_{ij}$  is the abundance of species  $j$  in plot  $i$ , and  $I_j$  indicates whether each species is an acidophyte ( $n_j = 1$ ) or not ( $n_j = 0$ ). By changing  $I_j$ , the same equation is applied for the neutrophyte and nitrophyte indices. These same indices have been used in related studies to assess N effects on lichen communities in the western US (Jovan, 2008; Jovan and McCune, 2006). Relationships between measurements of throughfall N ( $\text{NH}_4^+ + \text{NO}_3^-$ ), calculated indicator indices, and N concentration in *L. vulpina* were examined with simple linear least squares regression. Correlation strength was evaluated with coefficients of determination.

#### 2.4.2. Data integration

Canopy throughfall measurement points ( $n = 11$ ) were matched with nearby topographically similar sites where *L. vulpina* was analyzed for N in a previous pollution bioindication study (Jovan and Carlberg, 2007) and where epiphytic lichen communities were surveyed by the FIA between 1998 and 2003 (Jovan and McCune, 2006). Geographic distance from throughfall measurement points to sites where one or both of the lichen variables were measured ranged from <1 to 23 km (average 10 km). In three cases, *L. vulpina* and lichen community data were co-located. Although distance between the lichen plots and the throughfall plots were on average 10 km apart, on the scale of the Sierra Nevada Mountains, N deposition is expected to be highly similar between the paired plots within a given catchment. Lichen community data used in this analysis were restricted to plots dominated by conifers ( $\geq 85\%$  basal area) to decrease effects of stand composition on community composition.

#### 2.5. N as a nutrient CL determined from the simple mass balance steady state model

Theoretical critical loads were calculated using the SMB model to compare with the empirical CL determined for streamwater  $\text{NO}_3^-$ . According to the Critical Load Mapping Manual (MM; UNECE ICP, 2004) the following equation was used:  $\text{CL}_{\text{nut}}(\text{N}) = N_i + N_u + N_{\text{le}(\text{acc})}/(1 - f_{\text{de}})$ , where  $\text{CL}_{\text{nut}}(\text{N})$  is the critical load of nutrient N,  $N_i$  is the long-term immobilization of N in soil organic matter,  $N_u$  is the net removal of N in harvested vegetation and animals,  $N_{\text{le}(\text{acc})}$  is the acceptable leaching of N and  $f_{\text{de}}$  is the denitrification fraction. The  $N_{\text{le}(\text{acc})}$  term was calculated as the product of the precipitation surplus ( $Q$ ,  $\text{m}^3 \text{ ha}^{-1} \text{ year}^{-1}$ ) by the acceptable N concentration ( $[\text{N}]_{\text{acc}}$ ,  $\text{eq m}^{-3}$ ). Following MM prescriptions,  $N_i$  and  $[\text{N}]_{\text{acc}}$  were set to  $1 \text{ kg N ha}^{-1} \text{ year}^{-1}$  and  $0.2 \text{ mg N L}^{-1}$ , respectively, although calculations were also performed using  $3.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Downing et al., 1993) and  $3 \text{ mg N L}^{-1}$  (De Vries et al., 2007), respectively (Table 4) because these are considered to be more realistic values. To avoid negative  $Q$  values (precipitation surplus) that are often observed in Mediterranean systems, this term was calculated from the long term average flow volume of a perennial stream (USGS Monitoring Station no. 11063680) draining the Devil Canyon/Camp Paivika watershed ( $\sim 1600 \text{ m}^3 \text{ ha}^{-1} \text{ year}^{-1}$ ; USGS, 2007). Similarly  $N_u$  was considered to be 0 as recommended by the MM for long-term net uptake of unmanaged forests. Finally  $f_{\text{de}}$  was considered to be 0.1, as corresponds to sandy loam soils (Downing et al., 1993).

#### 2.6. DayCent biogeochemical model simulations

Critical loads were also calculated using the DayCent biogeochemistry simulation model. DayCent version 4.5 was used in this study to simulate historical N saturation symptoms such as N trace gas emissions from soil and  $\text{NO}_3^-$  leaching and to estimate the N deposition threshold for such losses. DayCent (Del Grosso et al., 2000; Parton et al., 1998, 2001) is the daily time step version of the CENTURY model (Parton et al., 1993). It simulates the biogeochemical processes of carbon, nitrogen, phosphorus, and sulfur associated with soil organic matter (SOM) in multiple ecosystem types. One feature of DayCent important to this study is the recent improvement of N cycling algorithms, including the simulation of  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$  emissions resulting from nitrification and denitrification. Other improvements relate to



Table 3  
Lichen species designation to three N indicator groups based on work by Jovan (2008)

Acidophytes	Neutrophytes	Nitrophytes	Other
<i>Alectoria sarmentosa</i>	<i>Melanelia elegantula</i>	<i>Candelaria concolor</i>	<i>Ahtiana sphaerosporella</i>
<i>Bryoria fremontii</i>	<i>M. exasperatula</i>	<i>Phaeophyscia orbata</i>	<i>Cetraria merrillii</i>
<i>Cetraria orbata</i>	<i>M. glabra</i>	<i>Physcia adscendens</i>	<i>Collema furfuraceum</i>
<i>C. pallidula</i>	<i>M. subelegantula</i>	<i>Physcia aipolia</i>	<i>C. nigrescens</i>
<i>C. platyphylla</i>	<i>M. subolivacea</i>	<i>Physcia stellaris</i>	<i>Letharia columbiana</i>
<i>Esslingeriana idahoensis</i>	<i>Parmelia hygrophila</i>	<i>Physcia tenella</i>	<i>L. vulpina</i>
<i>Evernia prunastri</i>	<i>P. sulcata</i>	<i>Xanthoria candelaria</i>	<i>Parmelina quercina</i>
<i>Hypogymnia enteromorpha</i>	<i>Physconia americana</i>	<i>X. fallax</i>	<i>Phaeophyscia ciliata</i>
<i>H. imshaugii</i>	<i>P. enteroxantha</i>	<i>X. fulva</i>	<i>Physcia biziana</i>
<i>H. metaphysodes</i>	<i>P. isidiigera</i>	<i>X. hasseana</i>	<i>Tholurna dissimilis</i>
<i>Nodobryoria abbreviata</i>	<i>P. perisidiosa</i>	<i>X. oregana</i>	
<i>N. oregana</i>		<i>X. polycarpa</i>	
<i>Platismatia glauca</i>			
<i>Usnea</i> spp.			

The N-sensitivities of species designated as “other” are unknown. Abundance of the species in the “other” group contributes to total lichen abundance as calculated for the indicator indices.

detailed soil N mineralization–immobilization processes associated with various organic matter pools (including microbial), which are distinguished by their decomposition rates. Required inputs to the model include daily maximum/minimum temperature and precipitation, site-specific soil properties and hydraulic characteristics, and current and historical land use. Model runs were initialized and stabilized by repeatedly using site-specific weather data for 900 years (i.e., initially started from 1000 AD), background N deposition ( $0.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ), and fire occurrence every 100 years. For the final model runs Daycent was set for the stand to regenerate after fire in 1901 and was run until 2060 without further fire occurrence, thus simulating the current conditions of fire suppression. The model provides approximations of historical tree growth, litter C, SOM and C/N ratios in the study area (Allen et al., 2007; Fenn et al., 2005; Grulke and Balduman, 1999; Grulke et al., 2001). Some DayCent parameters, mostly related to tree growth, N adsorption by litter, and decomposition of litter and the soil organic matter component referred to as the chemically-resistant fraction, were modified in order to achieve reasonably well-fitted outputs with observations of tree biomass and allocation, litter and soil organic matter accumulation, and C/N ratios.

The model was parameterized for a high (CP) and low (BF) deposition site with gradually increasing N deposition beginning in 1930 to the current throughfall N deposition levels ( $70$  and  $8.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$  at CP and BF, respectively). Inputs for the estimated historical rate of increase in N deposition since 1930 are shown in Table 5. Inasmuch as historical N deposition data are not available for the study sites, we estimated historical inputs and temporal patterns of deposition based on intermittent measurements at CP and BF (Fenn and Bytnerowicz, 1993, 1997; Fenn et al., 2000; Fenn and Poth, 2004; and M.E. Fenn unpublished data) and a number of early air pollution reports and historical data (Bytnerowicz et al., 2008; Cox et al., 2006; Egerton-Warburton et al., 2001). Ozone injury to herbaceous plants was first reported in the Los Angeles Basin in 1944 and by 1950 crop damage was documented in

Orange, Riverside and San Bernardino counties (Miller et al., 1963). Ozone injury to ponderosa pine was first reported in the San Bernardino Mountains near our CP study site in 1953, although the cause of the injury was not elucidated until 1960 (Ohmart, 1980). These early observations provided information as to when significant air pollution began to impact the San Bernardino Mountains.

N deposition was estimated for  $\text{NO}_x$  and  $\text{NH}_x$  and then their sum provided an estimate of total inorganic N deposition at our study sites. The  $\text{NO}_3/\text{NH}_4$  ratios in air quality and deposition data since the late 1980s at CP and BF (Bytnerowicz et al., 1999; Fenn et al., 2000; Fenn and Bytnerowicz, 1993, 1997; Fenn and Poth, 2004) were also used as guidelines in estimating historical deposition. Also taken into account were historical population growth trends and vehicle miles driven in the South Coast Air Basin and in Riverside and San Bernardino Counties (Cox et al., 2006). California Air Resources Board data on  $\text{NO}_x$  emissions since 1975 were also used for evaluating trends in  $\text{NO}_x$  deposition (Cox et al., 2006). Ozone concentration data at Crestline (immediately adjacent to CP) since 1963 (Bytnerowicz et al., 2008) were used as proxy for estimating temporal trends in  $\text{NO}_x$  deposition at CP.

Deposition of  $\text{NH}_x$  was based on periodic measurements of atmospheric  $\text{NH}_3$  taken from 1988 to 2005 at CP and BF (Bytnerowicz et al., 1999; A. Bytnerowicz, personal communication; Fenn and Bytnerowicz, 1993),  $\text{NH}_x$  deposition in branch rinses, throughfall, bulk deposition and fog (Fenn and Bytnerowicz, 1993, 1997; Fenn et al., 2000), historical livestock populations in the area (Chitjian et al., 2000; Luebs et al., 1973), the  $\text{NH}_3$  emissions inventory for the South Coast Air Basin (Chitjian et al., 2000) and reports on increasing  $\text{NH}_3$  emissions from vehicles equipped with three-way catalytic converters

Table 4  
Calculation of theoretical critical loads for nutrient N ( $\text{CL}_{\text{nut}}(\text{N})$ ) with the simple mass balance (SMB) steady state model<sup>a</sup>

Parameter	Mapping manual	Revised	Best estimates
N immobilization ( $N_i$ )	1.0	3.5	12
Denitrification fraction ( $f_{\text{de}}$ )	0.1	0.1	3
Acceptable N leachate concentration ( $[\text{N}]_{\text{le,acc}}$ )	0.3	4.8	2
Estimated $\text{CL}_{\text{nut}}(\text{N})$	1.4	8.8	17

<sup>a</sup> Units for the various parameters are as follows:  $N_i$  ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ );  $f_{\text{de}}$  (dimensionless);  $[\text{N}]_{\text{acc}}$  ( $\text{mg N l}^{-1}$ );  $\text{CL}_{\text{nut}}(\text{N})$  ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ ). The best estimates for the various parameters and the estimated CL are based on DayCent modeling, literature and empirical data. See text for a discussion how each of the sets of values were derived.

Table 5  
Estimated historical N deposition inputs to a high (CP) and low (BF) pollution forest site as used for DayCent simulation scenarios in estimating ecosystem responses to N deposition

Year	Camp Paivika (high N)			Barton Flats (low N)		
	Total N	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Total N	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$
1930	5	1	4	0.5	0.1	0.4
1940	12	2	10	2	0.4	1.6
1950	25	4	21	3	0.6	2.4
1960	35	8	27	4	0.8	3.2
1970	47	12	35	5	1.0	4.0
1980	65	20	45	6	1.2	4.8
1990	65	25	40	7	1.6	5.4
2000	70	30	40	8.8	3.7	5.1
2005	70	31	39	8.8	3.7	5.1

Values for 2000 and 2005 are from throughfall data measured at the sites over this time period.

(Baum et al., 2001; Chitjian et al., 2000). Deposition inputs of  $\text{NO}_x$  and  $\text{NH}_x$  at CP and BF from 2000 to 2005 are actual values for throughfall measurements during this period at the sites (Table 5; Fenn et al., 2003a; Fenn and Poth, 2004; and M.E. Fenn, unpublished data).

For model runs to estimate the CL for  $\text{NO}_3^-$  leaching, deposition was increased from a background level of  $0.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$  to  $3 \text{ kg N ha}^{-1} \text{ year}^{-1}$  in 1930 and increased linearly to  $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$  by 1940. In 1940, N deposition was set at 19 different levels for each site ranging from 10 to  $80 \text{ kg N ha}^{-1} \text{ year}^{-1}$  and maintained at these levels for simulations as long as 120 years in order to simulate dose responses to increasing N deposition. For model simulations using this set range of inputs and for model runs using historical N deposition, annual N deposition was set to vary randomly by  $<10\%$ . Simulations were also run with 40% reduced precipitation at CP. The effect of a 117% increase in precipitation was tested at BF by using CP precipitation levels at BF (annual average of  $105.9 \text{ cm}$  at CP vs.  $48.7 \text{ cm}$  at BF). The increased precipitation scenario was tested at BF to determine how much of the lower N loss patterns at BF compared to CP was due to the much lower precipitation at BF. Based on simulated occurrences of peak streamwater  $\text{NO}_3^-$  concentrations above the clean site threshold of  $0.2 \text{ mg L}^{-1}$  (see Section 2.2), we determined the beginning year and conditions under which CL exceedance began. We included a stipulation that the critical  $\text{NO}_3^-$  leachate concentration must be exceeded at least once every 10 years on average to consider the threshold exceeded. Spurious  $\text{NO}_3^-$  exceedances that occur rarely due to extreme climatic events for example, do not indicate a catchment above the CL by our definition.

### 3. Results

#### 3.1. Empirical critical load for nitrate leaching and fine root biomass

The gradient in throughfall N deposition at the study sites ranged from a relatively pristine site in the northern Sierra Nevada ( $1.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) to heavily polluted sites in the San Bernardino National Forest in southern California with deposition rates as high as  $33\text{--}71 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Table 1). Peak  $\text{NO}_3^-$  concentrations at 11 of these sites also varied, ranging from  $0.07$  to  $107 \mu\text{eq L}^{-1}$ . Based on the linear regression ( $r^2 = 0.98$ ) of streamwater  $\text{NO}_3^-$  vs. throughfall N deposition (Table 2), the N deposition at which the critical threshold  $\text{NO}_3^-$  concentration ( $14.3 \mu\text{eq L}^{-1}$ ) occurs is  $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ , which can be considered as the preliminary empirical threshold for  $\text{NO}_3^-$  leaching at these sites (95% confidence interval:  $15\text{--}19 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ). It should be noted that the unusually high correlation coefficient is possibly due to the occurrence of nine sites with N deposition somewhat clustered at less than  $20 \text{ kg ha}^{-1} \text{ year}^{-1}$  and two sites with deposition much greater than 20 ( $36$  and  $71 \text{ kg ha}^{-1} \text{ year}^{-1}$ ). A similar relationship was evaluated for bulk deposition and streamwater  $\text{NO}_3^-$  concentration ( $r^2 = 0.72$ ; Table 2). In this case, the estimated CL for bulk deposition of N was  $4.8 \text{ kg ha}^{-1} \text{ year}^{-1}$  (95% confidence interval:  $3.8\text{--}5.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ ).

Based on previously published root biomass data (Grulke et al., 1998) and throughfall and streamwater  $\text{NO}_3^-$  data from this study at the same sites, we found a 26% reduction in fine root biomass at a throughfall N deposition of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  and streamwater peak  $\text{NO}_3^-$  concentration of  $10.8 \mu\text{eq L}^{-1}$ ; Table 2). As mentioned previously, this is a very preliminary result because the root biomass, N deposition and streamwater data are from only three sites across the N

deposition gradient in the San Bernardino Mountains. These tentative results indicate that a significant reduction in fine root biomass occurred at the N deposition threshold ( $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) at which elevated  $\text{NO}_3^-$  leaching was observed and that approximately  $11 \mu\text{eq L}^{-1}$  can be considered as a tentative critical value for peak streamwater  $\text{NO}_3^-$  concentrations associated with standing root biomass reductions. Medium-sized roots were impacted to an even greater degree than fine roots during the early July root growth flush (Grulke et al., 1998), but since the effect was equally strong at the moderate deposition site compared to the most polluted site, an estimate of the CL for this effect was not possible.

#### 3.2. Litter C:N as a predictor of the N deposition CL

Litter C:N values ranged from 24.2 at Camp Paivika in the western San Bernardino Mountains to 39.7 at the relatively pristine Lassen National Park in the northern Sierra Nevada. Litter C:N values were highly correlated with both throughfall N ( $r^2 = 0.79$ , Table 2) and streamwater  $\text{NO}_3^-$  ( $r^2 = 0.74$ , Table 2). The linear regression predicted a litter C:N value of 34.1 at the critical peak streamwater  $\text{NO}_3^-$  level of  $14.3 \mu\text{eq L}^{-1}$ .

#### 3.3. Empirical critical loads for lichen responses

The relationship of N concentration in *L. vulpina* to throughfall N was approximated by a linear model (Fig. 4). Enhanced N in *L. vulpina*, defined as exceedance of the 1.0% N clean site threshold, corresponds with an empirical CL of  $3.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$  in throughfall (95% confidence interval:  $0.70\text{--}5.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ ). At this load, acidophytes, neutrophytes, and nitrophytes are predicted to comprise an average of about 40%, 21%, and 11% of lichen abundance,

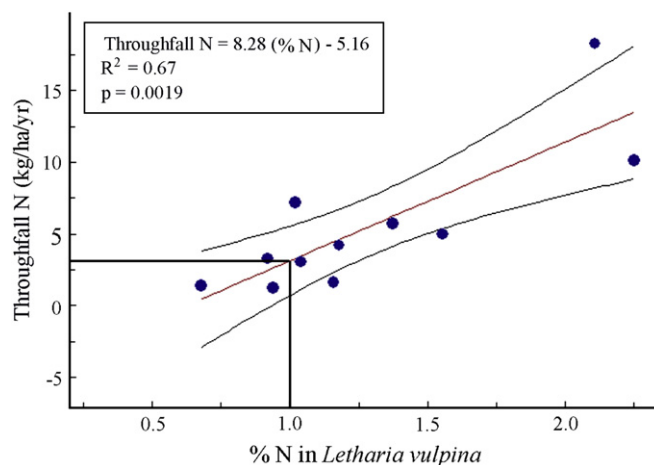


Fig. 4. Simple linear regression of canopy throughfall nitrogen (N) vs. % N (dry weight) in the epiphytic macrolichen *Letharia vulpina*. Lines on both sides of the fitted regression line are 95% confidence bands. The critical load ( $3.1 \text{ kg ha}^{-1} \text{ year}^{-1}$  of throughfall N) is the deposition of N at the clean site threshold of 1.0% N content in *L. vulpina* (95% confidence interval:  $0.70\text{--}5.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ ).

respectively. The nitrophyte contribution appears to depend also on hardwood basal area as discussed more below; the estimate presented here assumes a hardwood basal area of 0.

With increasing N in throughfall, N accumulation in *L. vulpina* increases and we witness a steady decline in the relative abundance of acidophytes in lichen communities (Fig. 5a and d). Based on the linear relationship between the acidophyte index and throughfall measurements, the relative abundance of acidophytes is predicted to decline by about 5.6% for every  $1 \text{ kg ha}^{-1} \text{ year}^{-1}$  increase in N deposition. In contrast, the relative abundance of neutrophytes is predicted to increase by about 3.2% for every  $1 \text{ kg ha}^{-1} \text{ year}^{-1}$  increase (Fig. 5b). This relationship is less clear than that of the acidophytes, although throughfall N still explains well over half of the variability in the neutrophyte index ( $r^2 = 0.58$ ). If we consider the response of both acidophyte and neutrophyte indicator groups in tandem, acidophyte dominance would likely shift to neutrophyte dominance when throughfall N reaches about  $5.2 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (95% inverse prediction interval:  $4.0\text{--}7.9 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ; Fig. 5c).

Proportion of nitrophyte abundance (PNA; data not shown) also increased with increasing N in throughfall deposition, although the correlation to throughfall data is much weaker than for the other two indicator groups ( $\text{PNA} = 0.029(\text{throughfall N}) + 0.0685$ ;  $r^2 = 0.33$ ,  $p = 0.06$ ). It is likely that this relationship is more variable due to the natural preference for and greater abundance of nitrophytes on hardwood

substrates, which were present in only four of the 11 sites. Inclusion of a variable that accounts for the proportion of stand basal area in hardwoods greatly improves the linear model ( $r^2 = 0.77$ ).

### 3.4. CL determined from simple mass balance

When the default parameterization of the SMB model for conifer species on a sandy loam soil was used (Table 4), which are very conservative values, a CL value of  $1.4 \text{ kg ha}^{-1} \text{ year}^{-1}$  of total N deposition was derived. However, when a new parameterization was carried out considering more realistic values provided in the literature for  $N_i$  (the long-term immobilization of N in soil organic matter) and  $[\text{N}]_{\text{le(acc)}}$  (the acceptable leaching of N), the original estimate was increased by more than 6 times to  $8.8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . Even this higher calculated estimate is well below the empirically derived CL of  $17 \pm 2 \text{ kg N ha}^{-1} \text{ year}^{-1}$  for peak streamwater  $\text{NO}_3^-$  concentrations and root biomass reduction.

### 3.5. CL information from the DayCent biogeochemical model

Based on historical N deposition scenarios and the criteria for  $\text{NO}_3^-$  threshold exceedance (peak streamwater  $\text{NO}_3^-$  above  $0.2 \text{ mg L}^{-1}$  at least once every 10 years on average), the threshold was first exceeded at CP around 1956 (Fig. 6b),

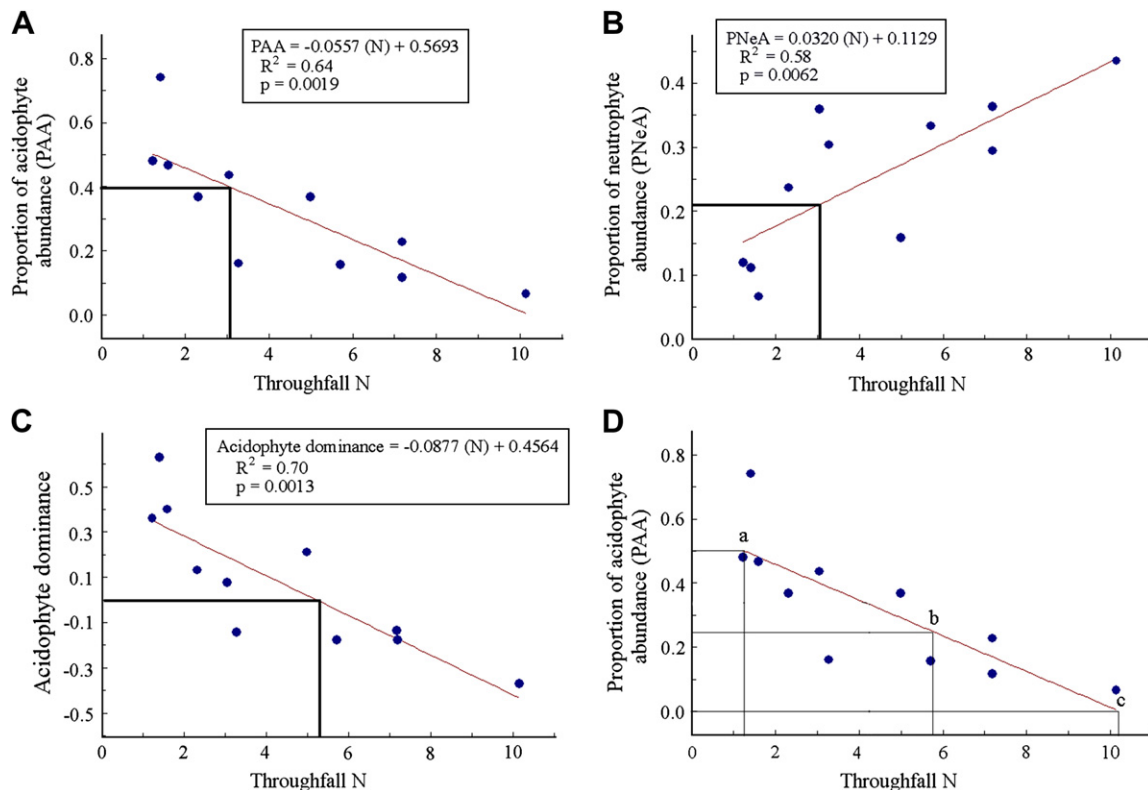


Fig. 5. Regressions of throughfall nitrogen ( $\text{kg N ha}^{-1} \text{ year}^{-1}$ ) and proportion of total lichen abundance in acidophytes (A and D), the proportion in neutrophytes (B), and the acidophyte dominance index (C). The critical load from Fig. 4 is shown in (A and B). Lines in frame (C) are the load corresponding with the shift from acidophyte to neutrophyte dominance ( $Y = 0$ ). (D) Three N loads corresponding with (a) lowest measurement of throughfall N in the dataset, (b) the load where half of relative acidophyte abundance is lost from the lichen community and (c) the load where all acidophytes are lost.



which is 16 years after elevated N deposition began in 1940. When deposition at CP was set at the empirical CL of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  beginning in 1940, streamwater  $\text{NO}_3^-$  did not exceed the threshold until 1978, a period of 38 years (Fig. 6a). With 40% reduced precipitation and N deposition set to  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ , elevated  $\text{NO}_3^-$  leaching did not occur at CP. With 40% reduced precipitation and historical N deposition inputs, the  $\text{NO}_3^-$  threshold was reached after 31 years in 1971 (Fig. 6b).

At BF, a constant N deposition of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  did not result in  $\text{NO}_3^-$  concentrations above the threshold except when precipitation was more than doubled by using the precipitation inputs from CP. In the latter case,  $\text{NO}_3^-$  leaching first exceeded the threshold after 16 years in 1956 (Fig. 6c). Nitrate leaching never exceeded the threshold at BF under historical N deposition rates, although when using the CP precipitation inputs peak  $\text{NO}_3^-$  concentrations were  $\geq 0.2 \text{ mg L}^{-1}$  on four occasions beginning in 1984 (Fig. 6d).

At the empirical CL, annual N export as  $\text{NO}_3^-$  peaked at  $1\text{--}2 \text{ kg ha}^{-1} \text{ year}^{-1}$  in high years at CP but values rarely reached  $1.0 \text{ kg ha}^{-1} \text{ year}^{-1}$  with 40% reduced precipitation (Fig. 7a). At the empirical CL at BF,  $\text{NO}_3^-$  export was always below  $0.5 \text{ kg ha}^{-1} \text{ year}^{-1}$  with normal precipitation (Fig. 7c). With doubled precipitation (CP precipitation levels) at BF  $\text{NO}_3^-$  export was sometimes greater than at CP (Fig. 7a,c). Under historical N deposition scenarios, elevated  $\text{NO}_3^-$  export began to occur regularly at CP (ranging from  $3$  to  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ )

after 1965, 25 years after elevated N deposition began (Fig. 7b). At BF historical N deposition did not affect  $\text{NO}_3^-$  export at either precipitation level, although  $\text{NO}_3^-$  export was increased from maximal values of  $0.2 \text{ kg ha}^{-1} \text{ year}^{-1}$  to  $0.5 \text{ kg ha}^{-1} \text{ year}^{-1}$  (and two points near  $1 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) when CP precipitation inputs were applied to the model (Fig. 7d).

At the empirical CL, annual gaseous losses of N showed an immediate response within the first year of increasing N deposition to  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  at both sites (Fig. 8a,c), and emissions were greater at BF (maximum values of  $9 \text{ kg ha}^{-1} \text{ year}^{-1}$  or greater near the latter years) than at CP (generally  $6 \text{ kg ha}^{-1} \text{ year}^{-1}$  or less). Under the estimated historical N deposition scenarios, current maximum values for gaseous N emissions at CP were approximately  $15 \text{ kg ha}^{-1} \text{ year}^{-1}$  compared to  $4 \text{ kg ha}^{-1} \text{ year}^{-1}$  at BF (Fig. 8b,d). Reduced precipitation significantly reduced gaseous emissions at CP, particularly at the empirical CL of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Fig. 8a). At BF increased precipitation had the effect of increasing interannual variation with the N deposition set at  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Fig. 8c).

The estimated N deposition threshold for  $\text{NO}_3^-$  leaching based on simulated  $\text{NO}_3^-$  concentrations in seepage water were  $17$  and  $30 \text{ kg ha}^{-1} \text{ year}^{-1}$  at CP and BF (Fig. 9a,b). This is based on N deposition occurring over a range of values for  $30\text{--}60$  years and with at least one occurrence per decade on average of a peak streamwater  $\text{NO}_3^-$  value over the  $0.2 \text{ mg L}^{-1}$  threshold. Increasing the time period of elevated N deposition resulted in lower threshold values. Reducing precipitation by 40% at CP

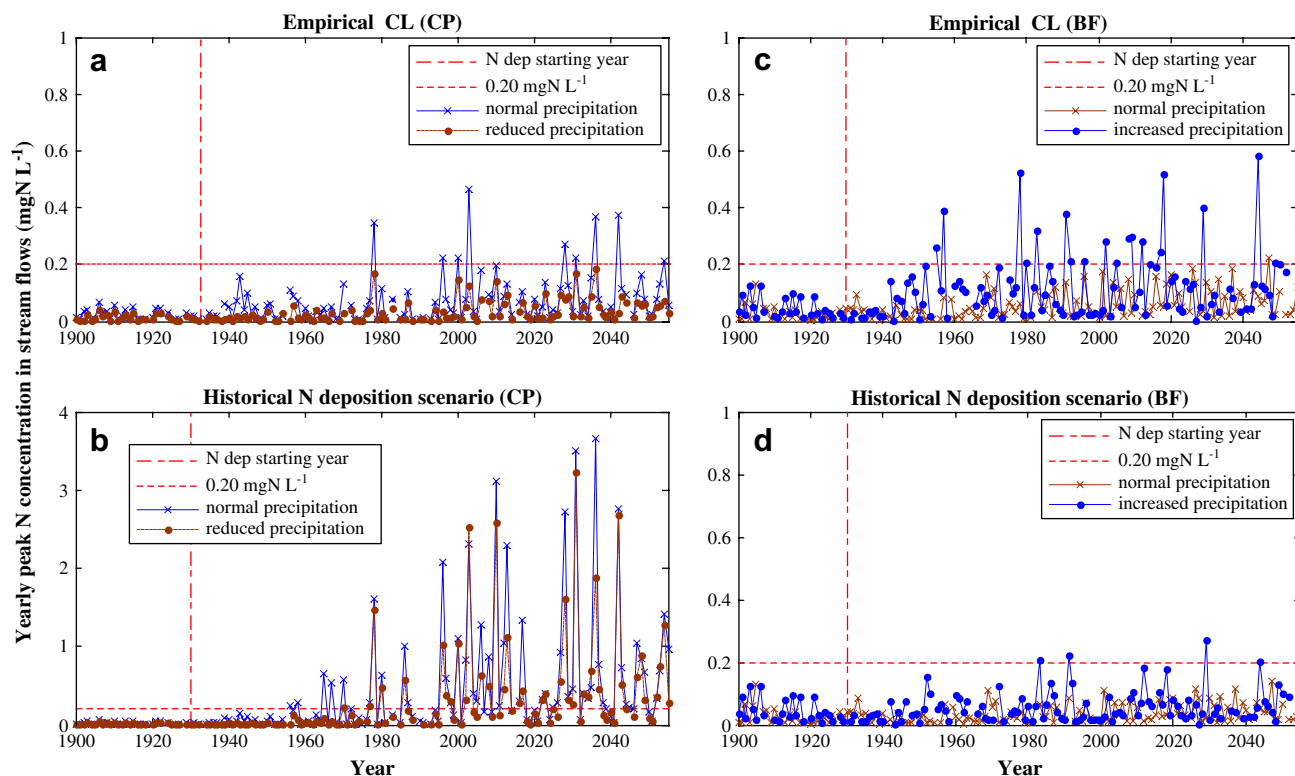


Fig. 6. DayCent simulated time trends of annual peak  $\text{NO}_3\text{-N}$  concentrations in streamwater under the N deposition rates of the empirical CL ( $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) and historical levels at the CP and BF sites in the San Bernardino National Forest. Total N deposition rates for each site were maintained at constant levels after the year 2000. Two precipitation scenarios were applied for each site. Normal refers to local precipitation levels. Reduced precipitation at CP represents a 40% reduction and increased precipitation at BF was achieved by increasing precipitation to that measured at CP, which represents a 117% increase for BF. Note that the y-axis scale for plot (b) differs from the other three plots.

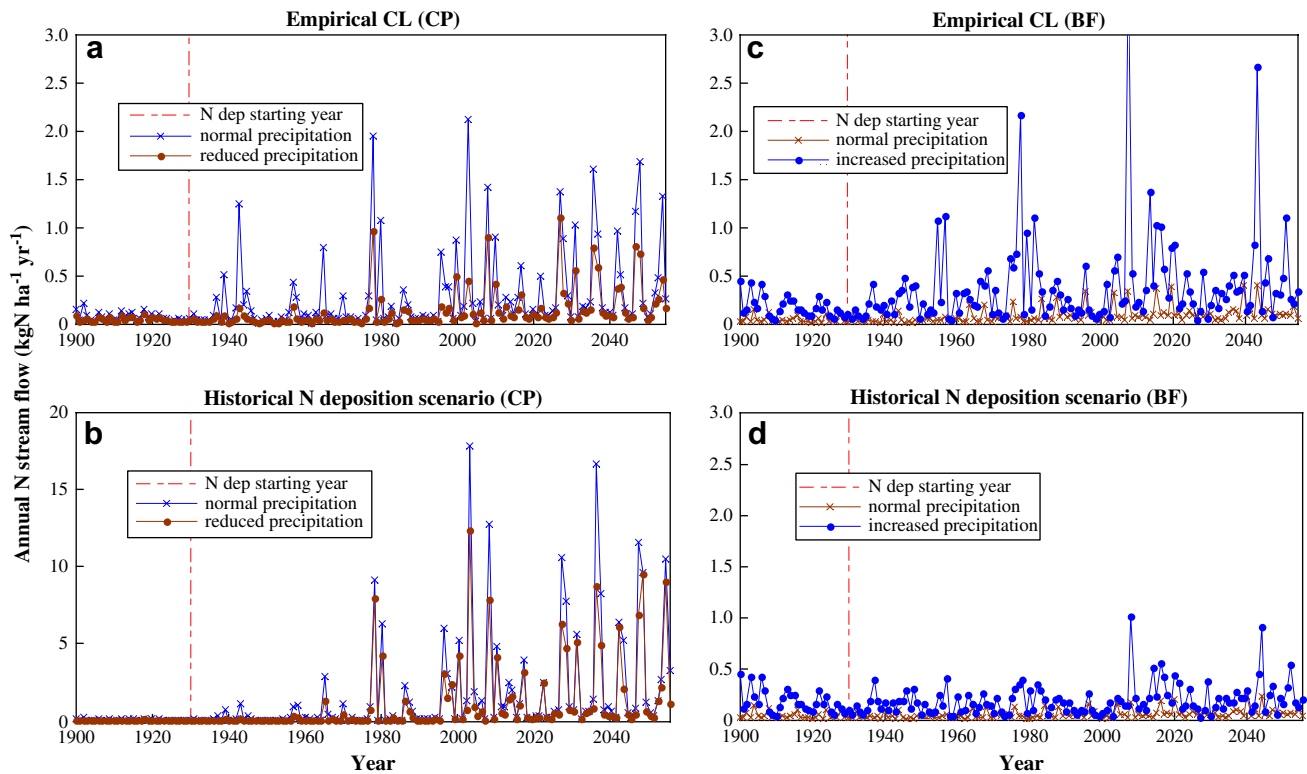


Fig. 7. DayCent simulated time trends of annual N gaseous emissions under the N deposition rates of the empirical CL ( $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) and historical levels at the CP and BF sites in the San Bernardino National Forest. Note that the y-axis scales differ among the plots. See Fig. 6 for a description of precipitation and N deposition scenarios.

resulted in an estimated threshold of  $20 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Fig. 9c), while doubling precipitation at BF, yielded a threshold of  $7 \text{ kg ha}^{-1} \text{ year}^{-1}$  over a 30–60 year time frame. The threshold at BF increased to  $16 \text{ kg ha}^{-1} \text{ year}^{-1}$  with doubled precipitation and a time frame of less than 30 years (Fig. 9d).

When considering annual  $\text{NO}_3^-$  export across a range of N deposition levels, increases in the mean and maximum  $\text{NO}_3^-$  export values were more responsive at CP than at BF at N deposition below  $55 \text{ kg ha}^{-1} \text{ year}^{-1}$ . At BF,  $\text{NO}_3^-$  export values increased slowly as a linear response with N deposition of  $10\text{--}55 \text{ kg ha}^{-1} \text{ year}^{-1}$ , then  $\text{NO}_3^-$  export at BF increased exponentially from  $55$  to  $80 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Fig. 10b,d). At current N deposition levels at CP ( $70 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) the simulated mean  $\text{NO}_3^-$  export is approximately  $2 \text{ kg N ha}^{-1} \text{ year}^{-1}$  after 30–60 years of N deposition, with a maximum  $\text{NO}_3^-$  export of approximately  $12 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Fig. 10a,c). At BF mean and maximum  $\text{NO}_3^-$  export values at approximately the current deposition (ca.  $10 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) and precipitation inputs were near 0 (Fig. 10b,d).

Patterns of simulated gaseous N emissions (annual mean and maximum values) in response to increasing N deposition were similar for the BF and CP sites, except that fluxes at BF were more than double of those at CP. At the empirical CL of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ , simulated mean gaseous losses of N were approximately 4.5 and 1.8 at BF and CP, respectively (Fig. 11a,b). With the critical value for mean annual N emissions over a 30–60 year period set at  $2 \text{ kg ha}^{-1} \text{ year}^{-1}$ , the threshold for N deposition would be 10 and  $20 \text{ kg ha}^{-1} \text{ year}^{-1}$  at BF and CP, respectively (Fig. 11a,b). If the critical

value for maximum annual N emissions is set at  $2 \text{ kg ha}^{-1} \text{ year}^{-1}$ , the threshold for N deposition would be 6 and  $13 \text{ kg ha}^{-1} \text{ year}^{-1}$  at BF and CP (Fig. 11c,d).

## 4. Discussion

### 4.1. Empirical CL for nitrate leaching and fine root biomass impacts

Elevated concentrations of streamwater  $\text{NO}_3^-$  is the cardinal sign of an N saturated ecosystem and a large amount of empirical data are available relating N deposition and  $\text{NO}_3^-$  export (Aber et al., 2003; Fenn and Poth, 1999; Gundersen et al., 2006; MacDonald et al., 2002; Van der Salm et al., 2007). The throughfall N deposition threshold established in this study for streamwater leaching of  $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$  is consistent with estimates from large European watershed surveys (Dise and Wright, 1995; Gundersen et al., 2006). Likewise, Stoddard et al. (2001) found that for catchments at stage 2 of N saturation (characterized by episodic elevated  $\text{NO}_3^-$  and high base-flow  $\text{NO}_3^-$  during the growing season; Stoddard, 1994), the average N deposition for the network of ICP Waters sites was ca.  $14 \text{ kg ha}^{-1} \text{ year}^{-1}$  (see Fig. 4 of their paper). Thus, general patterns for thresholds of N deposition leading to  $\text{NO}_3^-$  leaching losses are quite robust (MacDonald et al., 2002), although exceptions occur because varying environmental conditions and land use and management history can alter  $\text{NO}_3^-$  export patterns in relation to N deposition. The threshold for  $\text{NO}_3^-$  leaching of  $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$

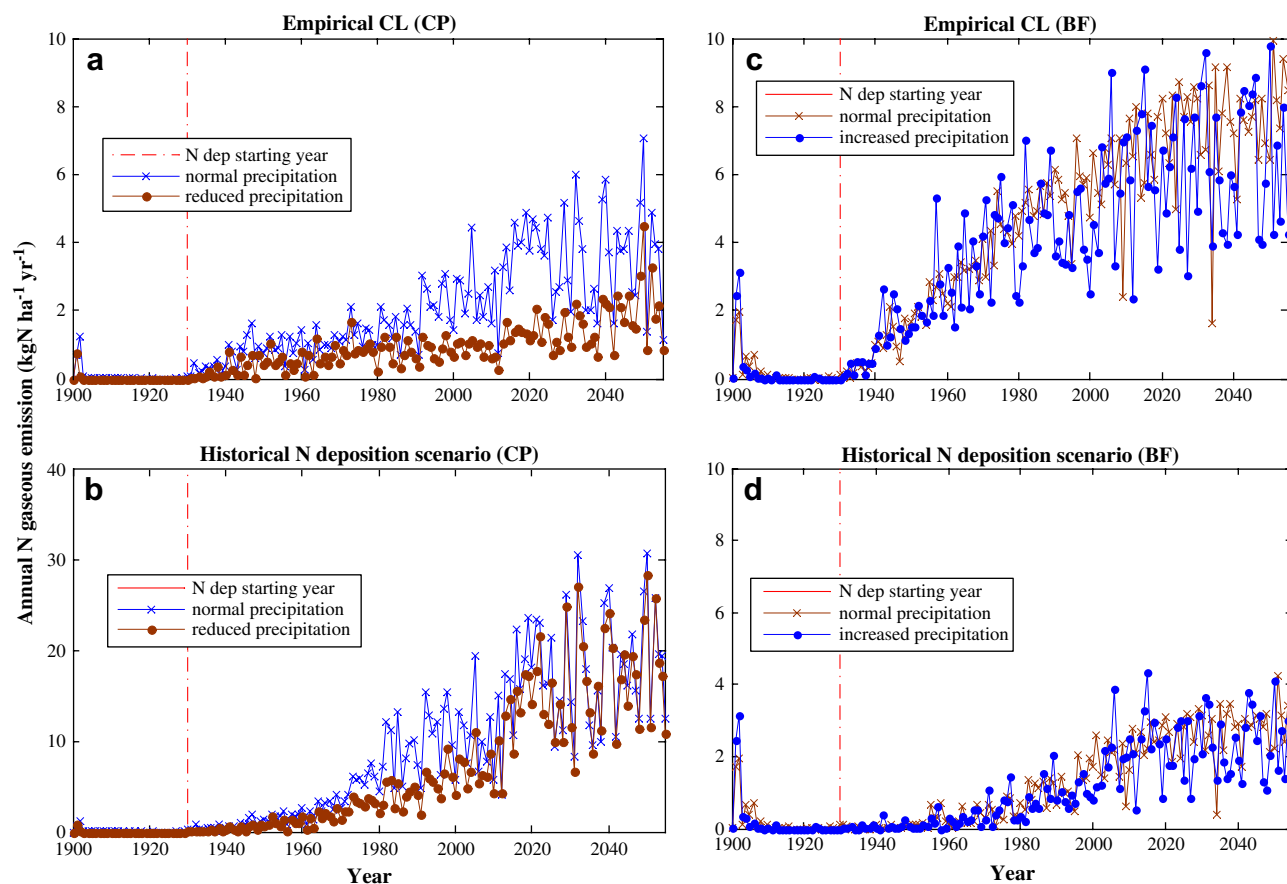


Fig. 8. DayCent simulated time trends of annual  $\text{NO}_3\text{-N}$  export in streamwater under the N deposition rates of the empirical CL ( $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) and historical levels the CP and BF sites in the San Bernardino National Forest. Note that the y-axis scale for plot (b) differs from the other three plots. See Fig. 6 for a description of precipitation and N deposition scenarios.

in this study is derived from and applicable to watersheds on predominantly granitic soils in the southwestern Sierra Nevada and the San Bernardino Mountains, yet results are highly similar to those from the temperate regions cited above. In the European ICP Forests network, data from Mediterranean climate watersheds were sometimes outliers (van der Salm et al., 2007), although data from these sites were under represented. Outliers were particularly apparent in mid-latitude and Mediterranean sites that receive moderate N deposition, have an above average temperature and relatively high C:N ratios of the organic layer (van der Salm et al., 2007), and probably had different precipitation patterns. Thus, the  $\text{NO}_3^-$  leaching response of the sites in our study appear to respond to N deposition similar to those of temperate forests and not to fit the profile of the outlier Mediterranean sites in the ICP Forests network receiving moderate N deposition.

A weakness in relating N deposition to streamwater  $\text{NO}_3^-$  export is that N deposition is usually only measured at one or at most a few points within the catchment and may not be representative of the entire catchment (Aber et al., 2003), whereas, streamwater  $\text{NO}_3^-$  concentrations are a result of N cycling, N deposition and hydrologic processes that occur over the entire catchment. Accuracy of empirical thresholds determined for  $\text{NO}_3^-$  leaching or other system-level responses may be improved by calibration with models that estimate N deposition

over the landscape (Weathers et al., 2006). Notwithstanding this scaling problem, however, the relationship between N deposition measured at select points and streamwater  $\text{NO}_3^-$  is useful for estimating the empirical threshold for an N saturation response (Aber et al., 2003). The lichen-based or fine root biomass CL can be determined from small plots, thus providing information at finer scales of resolution. The same can be done for  $\text{NO}_3^-$  leaching if sufficient soil solution or soil seepage samples are collected to reveal temporal patterns of  $\text{NO}_3^-$  loss, although installation and maintenance of replicate soil solution samplers would require considerable effort and cost.

Peak streamwater  $\text{NO}_3^-$  concentrations are observed during periods of high stream flow (Fenn and Poth, 1999; Riggan et al., 1985). In montane catchments in California with elevated N deposition, episodic  $\text{NO}_3^-$  concentrations exceed the  $\text{NO}_3^-$  threshold of  $14.3 \mu\text{M}$  ( $0.2 \text{ mg NO}_3\text{-N L}^{-1}$ ) during high flow events virtually every year. Peak concentrations in the more polluted sites in southern California are usually an order of magnitude greater than this threshold. In contrast,  $\text{NO}_3^-$  concentrations can be very low in mid-elevation conifer forests in California exposed to low or moderate N deposition. For example,  $\text{NO}_3^-$  concentrations in Log Creek, a perennial stream in a coniferous catchment in Sequoia National Park, peak  $\text{NO}_3^-$  concentrations were approximately  $1.0 \mu\text{M}$  over a 10-year period (Williams and Melack, 1997). The  $\text{NO}_3^-$



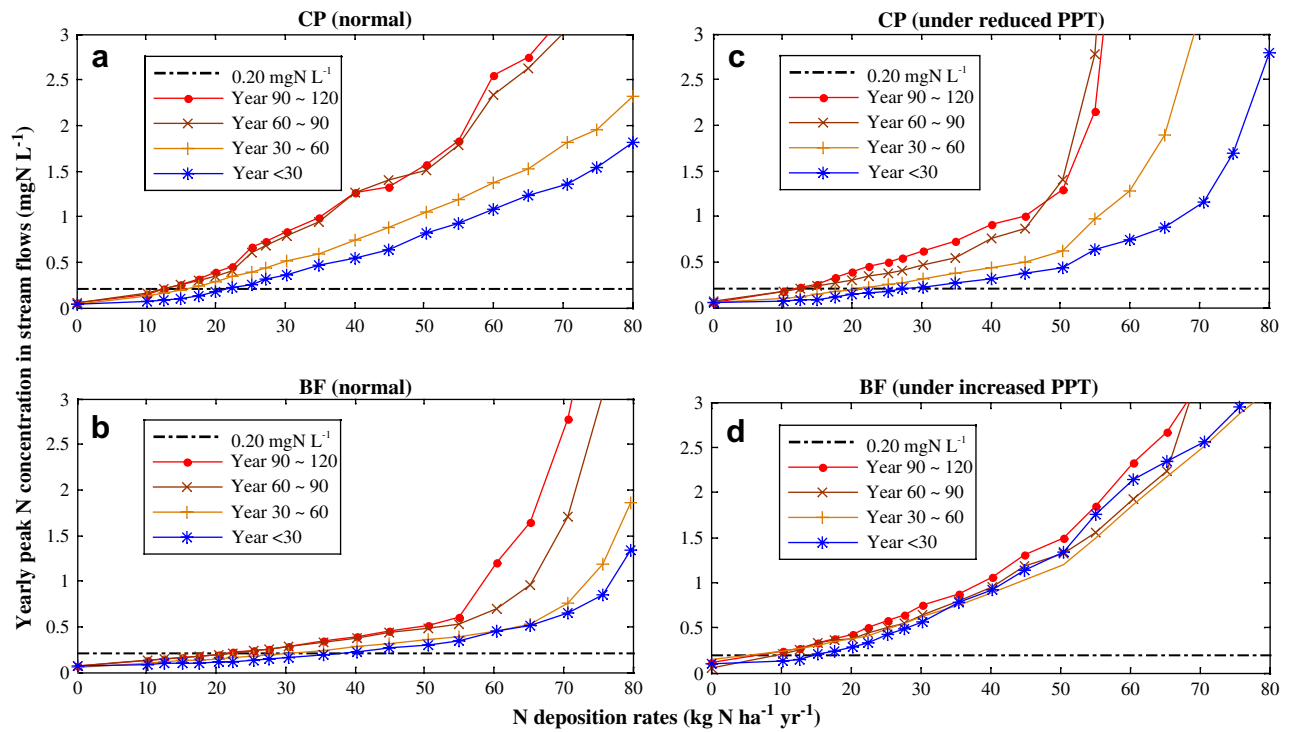


Fig. 9. DayCent simulated trends in annual peak  $\text{NO}_3\text{-N}$  concentrations in streamwater that occurred within various time periods since elevated N deposition began in 1940. In these simulations N deposition since 1940 ranged from 0 to  $80 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . The model was parameterized for the CP and BF sites in the San Bernardino National Forest. The prescribed N deposition values were set with  $<10\%$  random variation.

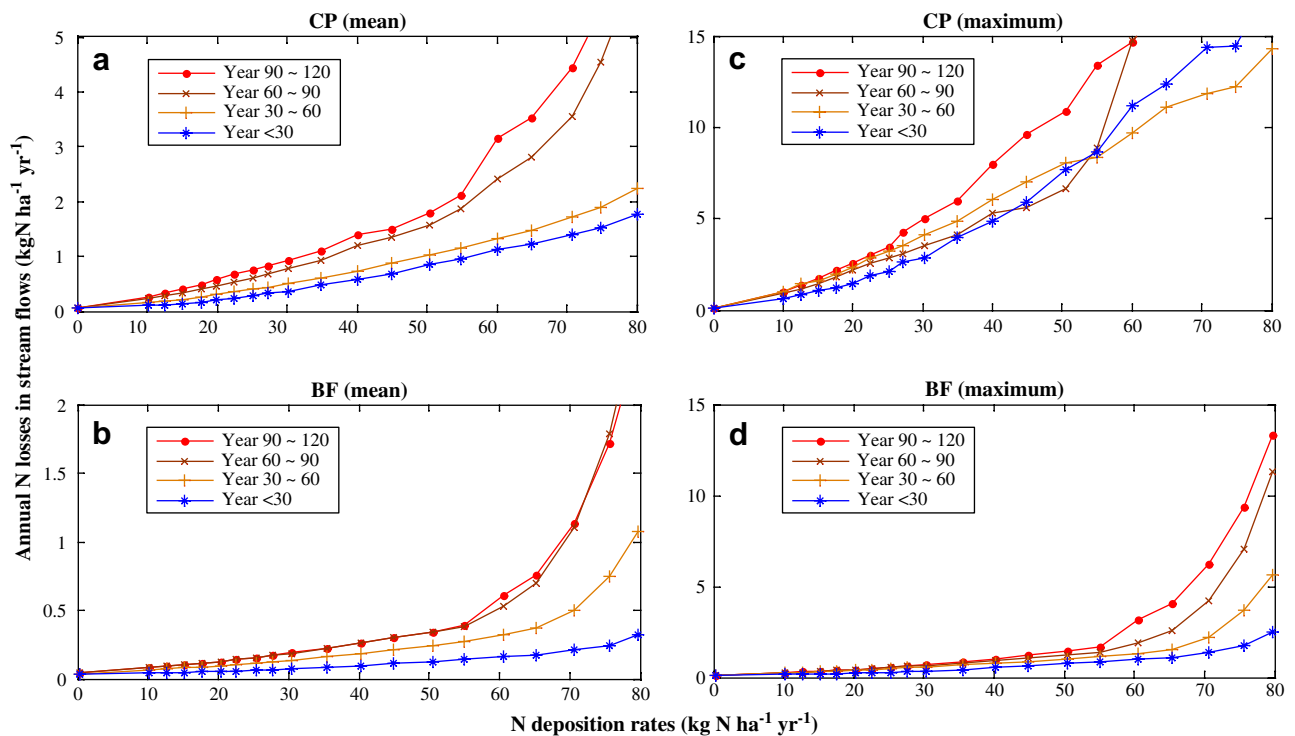


Fig. 10. DayCent simulated annual  $\text{NO}_3\text{-N}$  export in streamwater that occurred within various time periods since elevated N deposition began in 1940: (a) mean value at CP site, (b) mean value at BF site, (c) the max. values at CP site, and (d) the max. value at BF site. Note that the y-axis scales differ among the plots. See Fig. 9 for a description of N deposition scenarios.

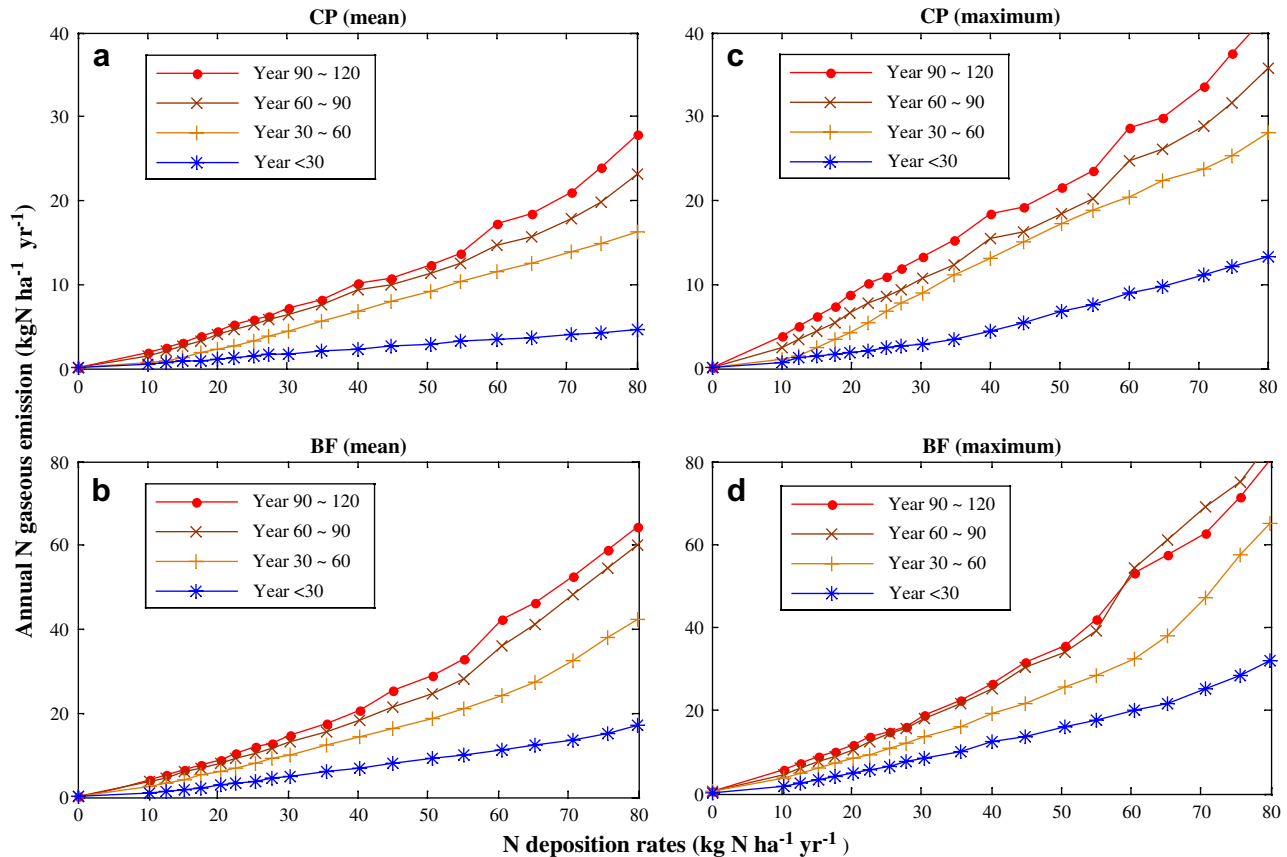


Fig. 11. DayCent simulated annual N gaseous emissions that occurred within various time periods since elevated N deposition began in 1940: (a) mean value at CP site, (b) mean value at BF site, (c) the maximum value at CP site, and (d) the maximum value at BF site. Note that the y-axis scales are different for CP and BF. See Fig. 9 for a description of N deposition scenarios.

threshold selected for peak  $\text{NO}_3^-$  runoff is a highly conservative value, indicative of watersheds at the incipient stage of the trajectory towards above-normal N losses from the system. Considering catchment surveys in North America and Europe, Gundersen et al. (2006) recommended an annual mean streamwater  $\text{NO}_3^-$  threshold of  $0.5 \text{ mg L}^{-1}$  ( $36 \text{ } \mu\text{M}$ ) as indicative of a “leaky” system. Because this is a mean value, it is not directly comparable to our peak  $\text{NO}_3^-$  value ( $14.3 \text{ } \mu\text{M}$  or  $0.2 \text{ mg NO}_3\text{-N L}^{-1}$ ), but the comparison indicates that the  $\text{NO}_3^-$  threshold derived for our study is a highly protective value for determining the empirical CL for streamwater  $\text{NO}_3^-$ .

However, using peak  $\text{NO}_3^-$  runoff concentrations has functional virtue because high runoff events are the period and process when the greatest sensitivity to ecosystem disturbance is apparent. Furthermore, seasonality is pronounced in these Mediterranean catchments and using annual means may make it difficult to detect incipient N saturation. The chosen peak  $\text{NO}_3^-$  threshold is based on reviews of “natural”  $\text{NO}_3^-$  leaching concentrations in relatively pristine catchments in Sweden (De Vries et al., 2007) and in many regions of North America (Fenn et al., 2002; Stoddard, 1994; Stottlemeyer and Hanson, 1989; Stottlemeyer and Toczydlowski, 1991; Williams et al., 1996), but with a particular emphasis on catchments in California (Chorover et al., 1994; Fenn and Poth, 1999; Meixner and Fenn, 2004; Riggen et al., 1985; Williams and Melack, 1997).

The previously documented negative response of standing fine root biomass in ponderosa pine across the air pollution gradient in the San Bernardino Mountains was used to estimate a preliminary N as a nutrient CL with linkage to a harmful biological effect. Establishment and quantification of the causal connection between N deposition or  $\text{NO}_3^-$  concentration in seepage water and a biological effect is often the most difficult step in determining the N CL (De Vries et al., 2007). The response of decreasing fine and medium root biomass with increasing air pollution exposure across the San Bernardino Mountains is a clear and dramatic response, although data were only collected at three sites from across the gradient (Grulke and Balduman, 1999; Grulke et al., 1998). Nitrogen deposition or greater N fertility (Nadelhoffer, 2000) and ozone (Grulke et al., 2001) are known to cause decreased fine root biomass and the observed response in the San Bernardino Mountains is thought to be a result of the combined effects of ozone and N enrichment. Although, the effects of ozone on fine root biomass can be considered as a confounding factor in determining a N deposition CL, we consider that the empirical CL for N should be determined under conditions of simultaneous exposure to ozone because in polluted California mixed conifer forests N deposition and ozone exposure are inseparable. The fine root biological response to N deposition and ozone is clear, but data from more sites are needed

to better quantify the response to N deposition. From currently available data we estimate that at the N deposition threshold for elevated  $\text{NO}_3^-$  leaching ( $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) standing fine root biomass is reduced by 26% during the early season root growth flush period (Grulke et al., 1998). Based on this preliminary evidence, we propose the N deposition threshold of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  for  $\text{NO}_3^-$  leaching as a first estimate of the CL associated with reduced fine root biomass in ponderosa pine in California mixed conifer forests.

#### 4.2. Predictors or indicators of CL exceedance for N as a nutrient

Like the European studies mentioned above (van der Salm et al., 2007), our results also illustrate that Mediterranean forests can have higher forest floor C:N ratios than temperate forests, even in N saturated sites. In temperate European forests the C:N threshold of 25 was a strong predictor of sites predisposed to high net nitrification rates and high levels of  $\text{NO}_3^-$  leaching under chronic N deposition, even with N deposition as low as  $10 \text{ kg ha}^{-1} \text{ year}^{-1}$  (Gundersen et al., 2006; MacDonald et al., 2002). In our study the critical value for litter C:N associated with elevated  $\text{NO}_3^-$  leaching was 34.1, 36% higher than in the European network and higher than an infertile red spruce site in Vermont where the onset of forest floor nitrification occurred below a C:N ratio of 31 (McNulty et al., 1991). In a survey of sites in northeastern North America, elevated net nitrification activity was correlated with C:N ratios between 20 and 25 (Aber et al., 2003), again indicating that forest floor C:N ratios are significantly higher in Mediterranean forests, even with elevated N deposition.

Breiner et al. (2007) reported that the critical value for foliar N in ponderosa pine at the N deposition threshold for streamwater  $\text{NO}_3^-$  leaching was equivalent to the critical level for foliar N (1.1% N) determined experimentally for ponderosa pine nutritional needs (Powers, 1981). By comparison, in European temperate forests the foliar N threshold was 1.4% and with an N concentration below this value,  $\text{NO}_3^-$  leaching did not occur (Gundersen et al., 2006). The relationship between N deposition and litter C:N or foliar N (Gundersen et al., 2006) and  $\text{NO}_3^-$  leaching suggests that these simple N status indicators can be used to identify sites where the CL is likely exceeded. These indicators are less temporally variable than streamwater  $\text{NO}_3^-$  and their implementation could be useful in locating areas at risk for the effects of excess N. However, the critical values indicative of CL exceedance for foliar N tend to be lower and values for litter C:N higher in southern California forests than in temperate forests in Europe and northeastern North America (Aber et al., 2003; Breiner et al., 2007; Gundersen et al., 2006; MacDonald et al., 2002). Further data are needed to see if this pattern holds for Mediterranean ecosystems in general (van der Salm et al., 2007).

#### 4.3. Empirical critical loads for lichen responses

We found evidence that a distinct shift in lichen community composition, from sensitive to more tolerant species, was in

progress at the N critical load of  $3.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . These community changes culminate in a shift away from the natural state of acidophyte dominance at a fairly moderate N load of  $5.2 \text{ kg ha}^{-1} \text{ year}^{-1}$ . The maintenance of healthy acidophyte populations is of particular concern because they are an integral part of food webs and are used as nesting material and habitat for insects, mollusks, birds, and animals, in the Sierra Nevada (McCune et al., 2007). The bearded lichen, *Bryoria fremontii* (Tuck.) Brodo & D. Hawksw., is an example of an acidophyte that serves as forage for a wide variety of species in our study region, including the northern flying squirrel (*Glaucomys sabrinus*), Douglas squirrel (*Tamiasciurus douglasii*), black-tailed deer (*Odocoileus hemionus*), and a variety of invertebrates (McCune et al., 2007). These foragers are themselves key parts of the diets of many insectivores and carnivores. A reduced abundance of acidophytes clearly has direct ecological consequence. Our data predict complete extirpation of acidophytes from the lichen community at an N load of about  $10.2 \text{ kg ha}^{-1} \text{ year}^{-1}$ . The midway benchmark in which the relative abundance of acidophytes in the lichen community is expected to drop by 50%, given the model, is  $5.7 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (note that even if no acidophytes are lost, a drop in relative abundance can still be caused by an increase in non-acidophytic species, which inflates the index denominator). At the other extreme, we see what could be an effect at even the lowest N levels; the N load that initiates acidophyte depression potentially lies outside the range of our data ( $<1.2 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) although more samples are needed from low N levels to better understand this relationship.

Our lichen CL of  $3.1 \text{ kg N ha}^{-1} \text{ year}^{-1}$  is much lower than those adopted by the UNECE for Europe ( $10\text{--}15 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) for lichens in temperate and boreal forests (Bobbink et al., 2003). However, the European CL range is primarily based on expert judgment (with an admitted shortage of lichen-based CL research), focuses on boreal forests, includes effects on algae, and the CL seems primarily based on extirpation of species. Bobbink et al. (2003) concluded that the disappearance of epiphytic lichen species from oak woodlands in Scotland and NW England in response to varying N deposition suggests a CL of  $11\text{--}18 \text{ kg ha}^{-1} \text{ year}^{-1}$ . Our prediction of extirpation of acidophytes at  $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ , falls within the European CL range for lichens in forests ( $10\text{--}15 \text{ kg ha}^{-1} \text{ year}^{-1}$ ; Bobbink et al., 2003), although we argue that these CL values are much too high if the CL allows sensitive and biologically valuable taxa to be extirpated from the forest.

Lichens (Fenn et al., 2003b, 2007; van Herk et al., 2003) and diatoms (Baron, 2006) appear to be the most sensitive terrestrial and aquatic responders to low levels of N enrichment. As such, lichens are useful bioindicators for determining a CL for terrestrial biotic community changes. Lichens can be considered as the “canary in the mine” or early warning indicators of biological change from air pollution, and N deposition in particular. In areas where the lichen CL is exceeded, biological effects are already occurring and further ecological impacts can be expected as N accumulates in the system and if N deposition increases. Based on the lichen CL



determined in this study, we conclude that known biological impacts on lichen communities are clearly occurring at N deposition levels as low as  $3\text{--}5\text{ kg N ha}^{-1}\text{ year}^{-1}$ . In California, this level of deposition or greater occurs over most of the forested region of the San Bernardino and San Gabriel Mountains, the western portions of the Sierra Nevada, and large areas of other mountain ranges in southern California. Critical load exceedance can be evaluated by either surveying the lichen community and employing the N indicator indices or by determining %N in *L. vulpina*.

#### 4.4. Simple mass balance CL

Theoretical critical loads for nutrient N were calculated using the steady state SMB approach (UNECE ICP, 2004). The calculated CL values ( $1.4$  and  $8.8\text{ kg N ha}^{-1}\text{ year}^{-1}$ ) were well below the empirical N deposition CL of  $17\text{ kg N ha}^{-1}\text{ year}^{-1}$  which leads to incipient  $\text{NO}_3^-$  leaching and approximately 25% fine root biomass reduction in these ecosystems. De Vries et al. (2007) concluded that the use of the critical N concentration in soil seepage water suggested in the UNECE manual is likely to lead to calculated CL lower than empirical values. Many uncertainties remain to be resolved to parameterize the SMB model, particularly in linking the impairment of soil-processes with biological impacts (UNECE ICP, 2004).

The DayCent results and field data (Fenn and Poth, 2001) suggest that trace gas N emissions, represented as the denitrification fraction calculated for the SMB model, are underestimated. Emissions of  $\text{NO}$ , largely a byproduct of enhanced nitrification rates in the upland forest and denitrification rates in the riparian zones, are important emissions sources not accounted for in the SMB calculations (Fenn et al., 1996; Fenn and Poth, 2001). DayCent and empirical data also suggest that acceptable leaching may be overestimated by the revised SMB model estimate (Table 4). The N immobilization term in the SMB model refers to long term N accumulation in soil organic matter and would appear to be underestimated, but no data from our sites are available to evaluate this. However, average N immobilization determined for the Nordic forests was  $8\text{ kg N ha}^{-1}\text{ year}^{-1}$  (De Vries et al., 2007), more than double our highest calculated value.

Another factor contributing to an underestimate of the calculated CL may be the enhanced N storage in the forest floor and in woody biomass and necromass at our sites as a result of the combined effects of ozone and chronic N deposition (Fenn et al., 2003c). These N pools are not normally considered within the N immobilization term of the SMB model and some N from these pools is slowly released via decomposition. In these summer dry Mediterranean ecosystems, litter decomposition is slow and recurring fire is normally a major N release mechanism (Johnson et al., 2008). However, because of long term fire suppression, N deposition and co-occurring ozone exposure, large pools of organic N accumulate in the forest floor and in woody material, suggesting that in a functional sense, N immobilization in our sites is likely much greater than the SMB model predicts (Fenn et al., 2003c, 2005). Our best estimates (from empirical

data, modeling and literature) of the terms used to derive the SMB CL are given in the final column of Table 4. Based on our best estimate of the empirical CL of  $17\text{ kg N ha}^{-1}\text{ year}^{-1}$ , we estimated by difference the N immobilization term to be  $12\text{ kg N ha}^{-1}\text{ year}^{-1}$ , compared to values of 1.0 and  $3.5\text{ kg N ha}^{-1}\text{ year}^{-1}$  using the original and revised SMB protocols (Table 4).

Another issue for Mediterranean forests is how the SMB model does not account for the potentially significant influence of forest management practices, prescribed fire, or wildfire events on plant nutrient uptake ( $N_u$ ) in wild or recreational areas. For instance, fire would likely produce a sharp increase in N CL because N uptake would be large in the early stages of regrowth and the ecosystem may not reach steady state if forest fires are recurring, especially considering that ponderosa pine forests may not reach an old growth steady state condition until 250 years (Law et al., 2003), far from the 100 years allowed in the SMB model to reach a steady-state condition. Also important for Mediterranean forests is the strong seasonality of N mobilization during wet season precipitation and runoff events leading to temporal extremes of increased risk of  $\text{NO}_3^-$  leaching. Another factor is large inter-annual variability from drought cycles that may last 4–7 years, which leads to boom or bust periods of N accumulation and release particularly if disturbance such as fire occurs (Riggan et al., 1994).

#### 4.5. DayCent model thresholds for N loss

The simulated estimate of the N deposition threshold for  $\text{NO}_3^-$  leaching at CP (high N deposition site) was  $17\text{ kg N ha}^{-1}\text{ year}^{-1}$  (same as the empirical estimate) compared to  $30\text{ kg N ha}^{-1}\text{ year}^{-1}$  at BF (low N deposition site). These results apply to model runs with elevated N deposition for 30–60 years, a time frame considered relevant to the historical period of N deposition in the region. Shorter periods of N deposition resulted in higher threshold values, while longer periods of N deposition yielded lower values.

A higher N deposition threshold for  $\text{NO}_3^-$  leaching at BF appears caused by lower precipitation at that site. When CP precipitation was used for BF, the threshold after 30–60 years of deposition was  $7\text{ kg N ha}^{-1}\text{ year}^{-1}$ . The threshold at BF (with CP precipitation) is lower than at CP presumably due to the lower plant and microbial biomass and thus lower N demand and retention capacity at BF. Thus, more N is available in soil with potential to be leached or emitted as trace gases.

It should be recognized that DayCent is not a watershed-scale model and the leached  $\text{NO}_3^-$  values actually represent  $\text{NO}_3^-$  concentrations in seepage water beneath the soil profile. Seepage water frequently has higher  $\text{NO}_3^-$  concentrations than streamwater because denitrification, particularly in the riparian zone and in-stream consumptive processes, can reduce  $\text{NO}_3^-$  concentrations (Gundersen et al., 2006). However, in some cases N deposition can enter the stream directly during snowmelt producing elevated concentrations not observed in seepage waters (Stoddard, 1994). For comparison purposes and because of the inherent uncertainty in the DayCent simulations, we are treating the  $\text{NO}_3^-$  leaching model outputs

as comparable to the empirical winter runoff  $\text{NO}_3^-$  data. In fact, the model results for CP under the normal precipitation and historical N deposition scenario show only 41% of the years from 1965 to 2005 where the  $\text{NO}_3^-$  concentrations exceed the threshold ( $14.3 \mu\text{M}$ ;  $0.2 \text{ mg NO}_3\text{-N L}^{-1}$ ). In contrast, streamwater  $\text{NO}_3^-$  concentration data from catchments draining the CP site far exceeded the threshold every year since 1995 when data were available (Fenn and Poth, 1999; Meixner and Fenn, 2004).

Under historical N deposition at CP, simulated threshold  $\text{NO}_3^-$  concentration was first exceeded at CP in 1956, 16 years after elevated deposition began in 1940. Thus, our best estimates are that elevated  $\text{NO}_3^-$  leaching, the cardinal symptom of a N saturated catchment, began around 1956. However, this may be a conservative estimate of the time to N saturation or CL exceedance considering that under the high N deposition loading at CP, the model underestimates peak  $\text{NO}_3^-$  concentrations in many years. Li et al. (2006) also reported that DayCent underestimated stream  $\text{NO}_3^-$  export in January in a small chaparral catchment in Sequoia National Park. The earliest field data in the region showing chronic  $\text{NO}_3^-$  leaching is from the San Dimas Experimental Forest in the San Gabriel Mountains. Streamwater  $\text{NO}_3^-$  concentrations and annual N export values similar to those near CP have been reported since 1979 (Riggan et al., 1985, 1994; Meixner et al., 2006). Because of the unusually high streamwater  $\text{NO}_3^-$  concentrations that have been reported for San Dimas since 1979 (as high as  $500 \mu\text{eq L}^{-1}$ ; Riggan et al., 1985) and the historically-elevated N deposition at San Dimas (Bytnerowicz et al., 1987), N saturation conditions likely developed there prior to the 1970s. Although the San Dimas data are from low-elevation chaparral catchments located closer to Los Angeles than our San Bernardino mountain sites, data from San Dimas support the estimation of N saturation conditions occurring in catchments in the Los Angeles Basin by around 1960 if not sooner. Considering that we estimate N deposition at CP to be  $35 \text{ kg ha}^{-1} \text{ year}^{-1}$  by 1960, this would not be an unexpected result.

Reduction of precipitation by 40% at CP was associated with pronounced reductions in streamwater  $\text{NO}_3^-$  concentrations and gaseous N losses when N deposition was set at the empirical N deposition threshold of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ . Streamwater  $\text{NO}_3^-$  concentrations were less affected under historical N deposition inputs, but gaseous losses of N at CP were greatly reduced by a 40% reduction in precipitation. The latter effect may be due to soil drying and less favorable conditions for nitrification and denitrification. Doubled precipitation at BF caused dramatic increase in  $\text{NO}_3^-$  leaching but mainly affected gaseous losses by increasing the interannual extremes. Thus, it seems that the greatest effect of increasing precipitation is to increase  $\text{NO}_3^-$  flushing and leaching from the soil profile at sites with moderate N deposition.

Gaseous losses of N in the model responded within the first 2 years in most cases to N deposition levels of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$  or greater. At BF under historical N deposition (currently  $8.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ ), trace gas emissions increased slowly and did not maintain elevated fluxes until around 1975, 35 years after deposition began. At CP and BF the percent of

N deposition re-emitted as N trace gases in the year 2000 according to DayCent was 20 and 22% respectively. These results agree with European studies demonstrating that temperate forests show increased NO and  $\text{N}_2\text{O}$  fluxes when throughfall N deposition was greater than  $15 \text{ kg ha}^{-1} \text{ year}^{-1}$  and that 17–20% of the atmospherically deposited N was re-emitted as NO and  $\text{N}_2\text{O}$  (Gasche and Papen, 2002; Skiba et al., 2004).

#### 4.6. Comparison of CL approaches

We consider the empirical approach to produce the most reliable estimates of N deposition CLs. As expected, the empirical CL for lichen effects ( $3\text{--}5 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) was much lower than for N saturation responses based on  $\text{NO}_3^-$  leaching or fine root biomass reduction (empirical value of  $17 \text{ kg ha}^{-1} \text{ year}^{-1}$ ) or gaseous N losses (DayCent simulated CL of 20 and  $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$  at the CP and BF sites, respectively). Lichen-based CL values can function as early warning sentinels because lichens respond to low levels of N deposition and the response is much more rapid than the broader biogeochemical cycle indicators such as foliar N, litter C:N or streamwater  $\text{NO}_3^-$  concentrations. This is not surprising, considering that lichens take up N exclusively from the atmosphere and have no means to regulate uptake.

The revised CL estimate from the SMB model was  $8.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ , which is similar to current N deposition at BF and approximately 50% lower than the empirical CL for fine root biomass and DayCent simulated and empirical thresholds for  $\text{NO}_3^-$  leaching. The forest at BF is still highly N-limited and exhibits highly conservative N cycling with no observable impacts on fine root biomass (Grulke et al., 1998). The SMB model needs further refinement to more accurately estimate the N as a nutrient CL in mixed conifer forests of California. Each of the component terms of the SMB model entails considerable uncertainty (Heywood et al., 2006).

The DayCent biogeochemical model simulations provided an estimate of the time to develop N saturation symptoms and also predicted N storage pool sizes associated with  $\text{NO}_3^-$  export. These types of predictions are difficult to make with empirical data because historical N deposition and  $\text{NO}_3^-$  export data are limited and it is difficult to collect N budget data from replicated sites across N deposition gradients. Empirical data from the CP and BF sites on streamwater  $\text{NO}_3^-$  export, trace gas emissions, and N pool sizes (Fenn and Poth, 1999, 2001; Fenn et al., 2005) indicate that the DayCent model produced reasonable simulations of the major N cycling processes. In summary, the two empirical CL approaches and the DayCent model each contributed useful information toward understanding CL for important ecosystem responses to chronic N deposition.

#### 4.7. Special considerations for Mediterranean ecosystems

Although the empirical and simulated thresholds for  $\text{NO}_3^-$  leaching were similar to values from northern temperate

forests, some characteristics of the Mediterranean forests in southern California may have an important influence on N loss and CL in these ecosystems. DayCent modeling results suggest that annual precipitation is an important factor affecting N losses as  $\text{NO}_3^-$  or as trace gas emissions.

The CL and N loss thresholds determined in this study were based on empirical and modeling results in the absence of fire for the last 100–160 years. However, these are ecosystems with estimated fire return intervals of 15–29 years in the absence of fire suppression (McBride and Laven, 1976), but possibly as long as 50 years (Minnich, 1999). Prescribed fire and particularly the wildfires that have occurred in some of these forests in recent years can have significant effects on stand condition and N cycling. These processes raise questions surrounding the forest steady state concept which is the basis for the SMB CL calculations. The strong seasonality of the Mediterranean climate is characterized by prolonged summer drought when N deposition accumulates on canopies and in the upper soil profile, followed by heavy winter rains that mobilize much of the accumulated N during the period of decreased plant N demand. This seasonality also suggests possible seasonal differences in the CL. The empirical and simulated  $\text{NO}_3^-$  leaching approach used in this study is based on peak  $\text{NO}_3^-$  concentrations in winter runoff and is designed to account for this seasonality. But further research is needed to evaluate the consequences of this strong seasonality in N fluxes on the harmful biological effects which CL are designed to prevent.

Another important factor possibly affecting the CL in our study sites is the co-occurrence of elevated ozone. Ozone causes major physiological disruption of the dominant pine species in these forests, reducing fine root biomass, altering water relations, and affecting nutrient uptake and allocation within the plant and the ecosystem (Fenn 2003c; Grulke and Balduman, 1999; Grulke et al., 1998), which can affect the CL for N as a nutrient. Ozone and N deposition also predispose trees to bark beetle attacks and mortality (Jones et al., 2004), which should ultimately be considered in CL evaluations as well, but data are needed from a greater number of sites.

#### 4.8. Management implications of CL findings

Simulated streamwater  $\text{NO}_3^-$  concentrations suggested that with longer deposition periods, the N deposition threshold leading to  $\text{NO}_3^-$  export decreases. For example, the simulated threshold at CP after 30–60 years of deposition was 17 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$  but decreased to 13 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$  after 90–120 years of N deposition. At BF, comparative threshold values were 30 and 22 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$ . This suggests that because N deposition has already been elevated for the past 60–70 years, future N deposition at N saturated sites such as CP will likely need to be reduced to less than 13 kg  $\text{ha}^{-1}$   $\text{year}^{-1}$  to return the ecosystem to a condition of conservative N cycling. It is still uncertain how many years N deposition levels would need to remain below a given threshold to restore forests to a conservative N cycle due to the current large N stores within these ecosystems.

DayCent simulations indicated that N losses from the ecosystem begin to accelerate when total forest N pools in soil, forest floor and living biomass reach ca. 2000 kg  $\text{ha}^{-1}$ . Nitrogen stocks at CP are estimated to be two to three times greater than this threshold (Arbaugh et al., 1999; Fenn et al., 2005). However, the model indicates that mineral soil N is the largest and most important N pool driving N losses, and that N losses as leached  $\text{NO}_3^-$  and as gaseous emissions accelerate above a threshold value of 1400 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$  at CP. Current N stores in the top 10 cm of the mineral soil at CP and BF are 1625 and 1390 kg  $\text{ha}^{-1}$ , respectively (Fenn et al., 2005). At CP, the N pool in the forest floor is of similar magnitude to the mineral soil and modeling results and field N cycling data for CP (Fenn et al., 2005) show that N losses are strongly related to N in the forest floor as well. Simulations suggest a threshold N pool in the forest floor associated with N loss of 450 kg N  $\text{ha}^{-1}$  compared to field values at CP and BF of 1370 and 580 kg N  $\text{ha}^{-1}$  (Fenn et al., 2005). These data and simulation results support the conclusion that N losses at CP will only be brought under control after N capital on the site has been reduced by a large but uncertain amount. Similarly, we estimate that N deposition may require as much as a five-fold reduction.

## 5. Conclusions

Our conservative, low critical load (3.1 kg  $\text{ha}^{-1}$   $\text{year}^{-1}$ ) for lichen responses is expected to protect the integrity of the lichen community, and thus preserve its ecological roles in the food web, nutrient cycling, and wildlife usage in conifer forests of the Sierra Nevada. Protecting lichens, the most sensitive ecosystem component, from adverse effects of N deposition also provides de facto protection for more tolerant ecosystem components. This lichen CL is exceeded over large portions of the western Sierra Nevada, including as far north as the Tahoe National Forest. Sensitive lichen species have been extirpated from polluted forest sites in the Los Angeles Basin, but because of steep N deposition gradients, concentrations of  $\text{NO}_3^-$  in surface runoff and groundwater are mainly impacted in regions at least partially exposed to corridors of polluted air mass transport. The empirical and simulated throughfall N deposition threshold for  $\text{NO}_3^-$  leaching in mixed conifer forests and the preliminary CL for a 26% reduction in fine root biomass is estimated at 17 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$ . This CL is exceeded in much of the western and central San Bernardino Mountains, along the southern face of the San Gabriel Mountains in the Los Angeles Air Basin, and in several areas of the southwestern Sierra Nevada Mountains. Simulation modeling results conservatively estimate that elevated  $\text{NO}_3^-$  leaching began in the late 1950s at a polluted site in the western San Bernardino Mountains, which corresponds with the first reports of foliar ozone injury at this site in 1953.

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